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(54) Title: LITHIUM-BASED ELECTROCHEMICALLY ACTIVE MATERIALS AND PREPARATION THEREOF

(57) Abstract: The invention provides novel lithium-mixed metal materials which, upon electrochemical interaction, release lithium ions, and are capable of reversibly cycling lithium ions. The invention provides a rechargeable lithium battery which comprises an electrode formed from the novel lithium-mixed metal materials. Methods for making the novel lithium-mixed metal materials and methods for using such lithium-mixed metal materials in electrochemical cells are also provided. The lithium-mixed metal materials comprise lithium and at least one other metal besides lithium. Preferred materials are lithium-mixed metal phosphates which contain lithium and two other metals besides lithium.

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LITHIUM-BASED ELECTROCHEMICALLY ACTIVE MATERIALS AND PREPARATION THEREOF

Field of the Invention

5   This invention relates to improved materials
usable as electrode active materials and to their
preparation.

Background of the Invention

          Lithium batteries are prepared from one or more
10   lithium electrochemical cells containing
electrochemically active (electroactive) materials. Such
cells typically include an anode (negative electrode), a
cathode (positive electrode), and an electrolyte
interposed between spaced apart positive and negative
15   electrodes. Batteries with anodes of metallic lithium
and containing metal chalcogenide cathode active material
are known. The electrolyte typically comprises a salt of
lithium dissolved in one or more solvents, typically
nonaqueous (aprotic) organic solvents. Other
20   electrolytes are solid electrolytes typically called
polymeric matrixes that contain an ionic conductive
medium, typically a metallic powder or salt, in
combination with a polymer that itself may be ionically
conductive which is electrically insulating. By
25   convention, during discharge of the cell, the negative
electrode of the cell is defined as the anode. Cells
having a metallic lithium anode and metal chalcogenide
cathode are charged in an initial condition. During
discharge, lithium ions from the metallic anode pass
30   through the liquid electrolyte to the electrochemical

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active (electroactive) material of the cathode whereupon
they release electrical energy to an external circuit.

It has recently been suggested to replace the
lithium metal anode with an insertion anode, such as a
5   lithium metal chalcogenide or lithium metal oxide.
Carbon anodes, such as coke and graphite, are also
insertion materials. Such negative electrodes are used
with lithium- containing insertion cathodes, in order to
form an electroactive couple in a cell. Such cells, in
10   an initial condition, are not charged. In order to be
used to deliver electrochemical energy, such cells must
be charged in order to transfer lithium to the anode from
the lithium- containing cathode. During discharge the
lithium is transferred from the anode back to the
15   cathode. During a subsequent recharge, the lithium is
transferred back to the anode where it re-inserts. Upon
subsequent charge and discharge, the lithium ions (Li$^+$)
are transported between the electrodes. Such
rechargeable batteries, having no free metallic species
20   are called rechargeable ion batteries or rocking chair
batteries. See U.S. Patent Nos. 5,418,090; 4,464,447;
4,194,062; and 5,130,211.

Preferred positive electrode active materials
include LiCoO$_2$, LiMn$_2$O$_4$, and LiNiO$_2$. The cobalt compounds
25   are relatively expensive and the nickel compounds are
difficult to synthesize. A relatively economical
positive electrode is LiMn$_2$O$_4$, for which methods of
synthesis are known. The lithium cobalt oxide (LiCoO$_2$),
the lithium manganese oxide (LiMn$_2$O$_4$), and the lithium
30   nickel oxide (LiNiO$_2$) all have a common disadvantage in
that the charge capacity of a cell comprising such
cathodes suffers a significant loss in capacity. That

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is., the initial capacity available (amp hours/gram) from
$LiMn_2O_4$, $LiNiO_2$, and $LiCoO_2$ is less than the theoretical
capacity because significantly less than 1 atomic unit of
lithium engages in the electrochemical reaction. Such an

5   initial capacity value is significantly diminished during
the first cycle operation and such capacity further
diminishes on every successive cycle of operation. For
$LiNiO_2$ and $LiCoO_2$ only about 0.5 atomic units of lithium
is reversibly cycled during cell operation. Many

10   attempts have been made to reduce capacity fading, for
example, as described in U.S. Patent No. 4,828,834 by
Nagaura et al. However, the presently known and commonly
used, alkali transition metal oxide compounds suffer from
relatively low capacity. Therefore, there remains the

15   difficulty of obtaining a lithium-containing electrode
material having acceptable capacity without disadvantage
of significant capacity loss when used in a cell.

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Summary of the Invention

The invention provides novel lithium-mixed
metal materials which, upon electrochemical interaction,
release lithium ions, and are capable of reversibly
cycling lithium ions. The invention provides a
rechargeable lithium battery which comprises an electrode
formed from the novel lithium-mixed metal materials.
Methods for making the novel lithium-mixed metal
materials and methods for using such lithium-mixed metal
materials in electrochemical cells are also provided.
The lithium-mixed metal materials comprise lithium and at
least one other metal besides lithium. Preferred
materials are lithium-mixed metal phosphates which
contain lithium and two other metals besides lithium.
Accordingly, the invention provides a rechargeable
lithium battery which comprises an electrolyte; a first
electrode having a compatible active material; and a
second electrode comprising the novel materials. In one
aspect, the novel materials are lithium-mixed metal
phosphates which preferably used as a positive electrode
active material, reversibly cycle lithium ions with the
compatible negative electrode active material. Desirably,
the lithium-mixed metal phosphate is represented by the
nominal general formula $Li_aMI_bMII_c(PO_4)_d$. Such compounds
include $Li_1MI_aMII_bPO_4$ and $Li_3MI_aMII_b(PO_4)_3$; therefore, in an
initial condition $0 \leq a \leq 1$ or $0 \leq a \leq 3$, respectively.
During cycling, x quantity of lithium is released where
$0 \leq x \leq a$. In the general formula, the sum of b plus c
is up to about 2. Specific examples are
$Li_1MI_{1-y}MII_yPO_4$ and $Li_3MI_{2-y}MII_y(PO_4)_3$.

In one aspect, MI and MII are the same. In a
preferred aspect, MI and MII are different from one

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another. At least one of MI and MII is an element
capable of an oxidation state higher than that initially
present in the lithium-mixed metal phosphate compound.
Correspondingly, at least one of MI and MII has more than
5   one oxidation state in the phosphate compound, and more
than one oxidation state above the ground state M^0. The
term oxidation state and valence state are used in the
art interchangeably.

In another aspect, both MI and MII may have
10   more than one oxidation state and both may be oxidizable
from the state initially present in the phosphate
compound. Desirably, MII is a metal or semi-metal having
a +2 oxidation state, and is selected from Groups 2, 12
and 14 of the Periodic Table. Desirably, MII is selected
15   from non-transition metals and semi-metals. In one
embodiment, MII has only one oxidation state and is
nonoxidizable from its oxidation state in the lithium-
mixed metal compound. In another embodiment, MII has
more than one oxidation state. Examples of semi-metals
20   having more than one oxidation state are selenium and
tellurium; other non-transition metals with more than one
oxidation state are tin and lead. Preferably, MII is
selected from Mg (magnesium), Ca (calcium), Zn (zinc), Sr
(strontium), Pb (lead), Cd (cadmium), Sn (tin), Ba
25   (barium), and Be (beryllium), and mixtures thereof. In
another preferred aspect, MII is a metal having a +2
oxidation state and having more than one oxidation state,
and is oxidizable from its oxidation state in lithium-
mixed metal compound.

30   Desirably, MI is selected from Fe (iron), Co
(cobalt), Ni (nickel), Mn (manganese), Cu (copper), V
(vanadium), Sn (tin), Ti (titanium), Cr (chromium), and

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mixtures thereof. As can be seen, MI is preferably
selected from the first row of transition metals and
further includes tin, and MI preferably initially has a
+2 oxidation state.

5   In a preferred aspect, the product $LiMI_{1-y}MII_yPO_4$
is an olivine structure and the product $Li_3MI_{1-y}(PO_4)_3$ is a
rhombohedral or monoclinic Nasicon structure. In another
aspect, the term "nominal formula" refers to the fact
that the relative proportion of atomic species may vary
10   slightly on the order of 2 percent to 5 percent, or more
typically, 1 percent to 3 percent. In still another
aspect, any portion of P (phosphorous) may be substituted
by Si (silicon), S (sulfur), and/or As (arsenic); and any
portion of O (oxygen) may be substituted by halogen,
15   preferably F (fluorine). These aspects are also
disclosed in U.S. Patent Application Serial Numbers
09/105,748 filed June 26, 1998, and 09/274,371 filed
March 23, 1999; and in U.S. Patent No. 5,871,866 issued
February 16, 1999, which is incorporated by reference in
20   its entirety; each of the listed applications and patents
are co-owned by the assignee of the present invention.

           The metal phosphates are alternatively
represented by the nominal general formulas such as
$Li_{1-x}MI_{1-y}MII_yPO_4$ (0 ≤ x ≤ 1), and $Li_{3-x}MI_{2-y}MII_y(PO_4)_3$
25   signifying capability to release and reinsert lithium.
The term "general" refers to a family of compounds, with
M, x and y representing variations therein. The
expressions 2-y and 1-y each signify that the relative
amount of MI and MII may vary. In addition, as stated
30   above, MI may be a mixture of metals meeting the earlier
stated criteria for MI. In addition, MII may be a
mixture of metallic elements meeting the stated criteria

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for MII.   Preferably, where MII is a mixture, it is a
mixture of 2 metallic elements; and where MI is a
mixture, it is a mixture of 2 metals.   Preferably, each
such metal and metallic element has a +2 oxidation state
5   in the initial phosphate compound.

        The active material of the counter electrode is
any material compatible with the lithium-mixed metal
phosphate of the invention.   Where the lithium-mixed
metal phosphate is used as a positive electrode active
10   material, metallic lithium, lithium-containing material,
or non-lithium-containing material may be used as the
negative electrode active material.   The negative
electrode is desirably a nonmetallic insertion material.
Desirably, the negative electrode comprises an active
15   material from the group consisting of metal oxide,
particularly transition metal oxide, metal chalcogenide,
carbon, graphite, and mixtures thereof.   It is preferred
that the anode active material comprises a carbonaceous
material such as graphite.   The lithium-mixed metal
20   phosphate of the invention may also be used as a negative
electrode material.

        In another embodiment, the present invention
provides a method of preparing a compound of the nominal
general formula $Li_aMI_bMII_c(PO_4)_d$ where $0 < a \le 3$; the sum
25   of b plus c is greater than zero and up to about 2; and
$0 < d \le 3$.   Preferred compounds include $Li_3MI_bMII_c(PO_4)_3$
where b plus c is about 2; and $LiMI_bMII_cPO_4$ where b plus c
is about 1.   The method comprises providing starting
materials in particle form.   The starting (precursor)
30   materials include a lithium-containing compound, one or
more metal containing compounds, a compound capable of
providing the phosphate $(PO_4)^{-3}$ anion, and carbon.

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Preferably, the lithium-containing compound is in
particle form, and an example is lithium salt.
Preferably, the phosphate-containing anion compound is in
particle form, and examples include metal phosphate salt
5   and diammonium hydrogen phosphate (DAHP) and ammonium
dihydrogen phosphate (ADHP). The lithium compound, one
or more metal compounds, and phosphate compound are
included in a proportion which provides the stated
nominal general formula. The starting materials are
10   mixed together with carbon, which is included in an
amount sufficient to reduce the metal ion of one or more
of the metal-containing starting materials without full
reduction to an elemental metal state. Excess quantities
of carbon and one or more other starting materials (i.e.,
15   5 to 10% excess) may be used to enhance product quality.
A small amount of carbon, remaining after the reaction,
functions as a conductive constituent in the ultimate
electrode formulation. This is an advantage since such
remaining carbon is very intimately mixed with the
20   product active material. Accordingly, large quantities of
excess carbon, on the order of 100% excess carbon are
useable in the process. The carbon present during
compound formation is thought to be intimately dispersed
throughout the precursor and product. This provides many
25   advantages, including the enhanced conductivity of the
product. The presence of carbon particles in the
starting materials is also thought to provide nucleation
sites for the production of the product crystals.

        The starting materials are intimately mixed and
30   then reacted together where the reaction is initiated by
heat and is preferably conducted in a nonoxidizing, inert
atmosphere, whereby the lithium, metal from the metal
compound(s), and phosphate combine to form the

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$Li_aMI_bMII_c(PO_4)_d$ product. Before reacting the compounds, the particles are intermingled to form an essentially homogeneous powder mixture of the precursors. In one aspect, the precursor powders are dry-mixed using a ball mill, such as zirconia media. Then the mixed powders are pressed into pellets. In another aspect, the precursor powders are mixed with a binder. The binder is selected so as to not inhibit reaction between particles of the powders. Therefore, preferred binders decompose or evaporate at a temperature less than the reaction temperature. Examples include mineral oils (i.e., glycerol, or C-18 hydrocarbon mineral oil) and polymers which decompose (carbonize) to form a carbon residue before the reaction starts, or which evaporate before the reaction starts. In still another aspect, intermingling is conducted by forming a wet mixture using a volatile solvent and then the intermingled particles are pressed together in pellet form to provide good grain-to-grain contact.

Although it is desired that the precursor compounds be present in a proportion which provides the stated general formula of the product, the lithium compound may be present in an excess amount on the order of 5 percent excess lithium compared to a stoichiometric mixture of the precursors. And the carbon may be present at up to 100% excess compared to the stoichiometric amount. The method of the invention may also be used to prepare other novel products, and to prepare known products. A number of lithium compounds are available as precursors, such as lithium acetate $(LiOOCCH_3)$, lithium hydroxide, lithium nitrate $(LiNO_3)$, lithium oxalate $(Li_2C_2O_4)$, lithium oxide (Li_2O), lithium phosphate (Li_3PO_4), lithium dihydrogen phosphate (LiH_2PO_4), lithium

vanadate ($LiVO_3$), and lithium carbonate (Li_2CO_3). The
lithium carbonate is preferred for the solid state
reaction since it has a very high melting point and
commonly reacts with the other precursors before melting.

5   Lithium carbonate has a melting point over 600°C and it
decomposes in the presence of the other precursors and/or
effectively reacts with the other precursors before
melting. In contrast, lithium hydroxide melts at about
400°C. At some reaction temperatures preferred herein of

10   over 450°C the lithium hydroxide will melt before any
significant reaction with the other precursors occurs to
an effective extent. This melting renders the reaction
very difficult to control. In addition, anhydrous LiOH
is highly hygroscopic and a significant quantity of water

15   is released during the reaction. Such water needs to be
removed from the oven and the resultant product may need
to be dried. In one preferred aspect, the solid state
reaction made possible by the present invention is much
preferred since it is conducted at temperatures at which

20   the lithium-containing compound reacts with the other
reactants before melting. Therefore, lithium hydroxide
is useable as a precursor in the method of the invention
in combination with some precursors, particularly the
phosphates. The method of the invention is able to be

25   conducted as an economical carbothermal-based process
with a wide variety of precursors and over a relatively
broad temperature range.

The aforesaid precursor compounds (starting
materials) are generally crystals, granules, and powders

30   and are generally referred to as being in particle form.
Although many types of phosphate salts are known, it is
preferred to use diammonium hydrogen phosphate $(NH_4)_2HPO_4$
(DAHP) or ammonium dihydrogen phosphate $(NH_4)H_2PO_4$ (ADHP).

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Both ADHP and DAHP meet the preferred criteria that the precursors decompose in the presence of one another or react with one another before melting of such precursor. Exemplary metal compounds are Fe_2O_3, Fe_3O_4, V_2O_5, VO_2, $LiVO_3$, NH_4VO_3, $Mg(OH)_2$, Cao, MgO, $Ca(OH)_2$, MnO_2, Mn_2O_3, $Mn_3(PO_4)_2$, CuO, SnO, SnO_2, TiO_2, Ti_2O_3, Cr_2O_3, PbO_2, PbO, $Ba(OH)_2$, BaO, $Cd(OH)_2$. In addition, some starting materials serve as both the source of metal ion and phosphate, such as $FePO_4$, $Fe_3(PO_4)_2$, $Zn_3(PO_4)_2$, and $Mg_3(PO_4)_2$. Still others contain both lithium ion and phosphate such as Li_3PO_4 and LiH_2PO_4. Other exemplary precursors are H_3PO_4 (phosphoric acid); and P_2O_5 (P_4O_{10}) phosphoric oxide; and HPO_3 meta phosphoric acid, which is a decomposition product of P_2O_5. If it is desired to replace any of the oxygen with a halogen; such as fluorine, the starting materials further include a fluorine compound such as LiF. If it is desired to replace any of the phosphorous with silicon, then the starting materials further include silicon oxide (SiO_2). Similarly, ammonium sulfate in the starting materials is useable to replace phosphorus with sulfur.

The starting materials are available from a number of sources. The following are typical. Vanadium pentoxide of the formula V_2O_5 is obtainable from any number of suppliers including Kerr McGee, Johnson Matthey, or Alpha Products of Davers, Massachusetts. Vanadium pentoxide has a CAS number of 1314-62-1. Iron oxide Fe_3O_3 is a common and very inexpensive material available in powder form from the same suppliers. The other precursor materials mentioned above are also available from well known suppliers, such as those listed above.

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The method of the invention may also be used to
react starting materials in the presence of carbon to
form a variety of other novel products, such as gamma-
LiV$_2$O$_5$ and also to produce known products. Here, the

5   carbon functions to reduce metal ion of a starting metal
compound to provide a product containing such reduced
metal ion. The method is particularly useful to also add
lithium to the resultant product, which thus contains the
metallic element ions, namely, the lithium ion and the

10   other metal ion, thereby forming a mixed metal product.
An example is the reaction of vanadium pentoxide (V$_2$O$_5$)
with lithium carbonate in the presence of carbon to form
gamma-LiV$_2$O$_5$. Here the starting metal ion V^{+5}V^{+5} is
reduced to V^{+4}V^{+5} in the final product. A single phase

15   gamma-LiV$_2$O$_5$ product is not known to have been directly
and independently formed before.

As described earlier, it is desirable to
conduct the reaction at a temperature where the lithium
compound reacts before melting. The temperature should

20   be about 400°C or greater, and desirably 450°C or
greater, and preferably 500°C or greater, and generally
will proceed at a faster rate at higher temperatures.
The various reactions involve production of CO or CO$_2$ as
an effluent gas. The equilibrium at higher temperature

25   favors CO formation. Some of the reactions are more
desirably conducted at temperatures greater than 600°C;
most desirably greater than 650°C; preferably 700°C or
greater; more preferably 750°C or greater. Suitable
ranges for many reactions are about 700 to 950°C, or

30   about 700 to 800°C.

Generally, the higher temperature reactions
produce CO effluent and the stoichiometry requires more

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carbon be used than the case where CO_2 effluent is
produced at lower temperature. This is because the
reducing effect of the C to CO_2 reaction is greater than
the C to CO reaction. The C to CO_2 reaction involves an
5   increase in carbon oxidation state of +4 (from 0 to 4)
and the C to CO reaction involves an increase in carbon
oxidation state of +2 (from ground state zero to 2).
Here, higher temperature generally refers to a range of
about 650°C to about 1000°C and lower temperature refers
10   to up to about 650°C. Temperatures higher than 1200°C
are not thought to be needed.

In one aspect, the method of the invention
utilizes the reducing capabilities of carbon in a unique
and controlled manner to produce desired products having
15   structure and lithium content suitable for electrode
active materials. The method of the invention makes it
possible to produce products containing lithium, metal
and oxygen in an economical and convenient process. The
ability to lithiate precursors, and change the oxidation
20   state of a metal without causing abstraction of oxygen
from a precursor is heretofore unexpected. These
advantages are at least in part achieved by the
reductant, carbon, having an oxide whose free energy of
formation becomes more negative as temperature increases.
25   Such oxide of carbon is more stable at high temperature
than at low temperature. This feature is used to produce
products having one or more metal ions in a reduced
oxidation state relative to the precursor metal ion
oxidation state. The method utilizes an effective
30   combination of quantity of carbon, time and temperature
to produce new products and to produce known products in
a new way.

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Referring back to the discussion of
temperature, at about 700°C both the carbon to carbon
monoxide and the carbon to carbon dioxide reactions are
occurring. At closer to 600°C the C to CO_2 reaction is
5   the dominant reaction. At closer to 800°C the C to CO
reaction is dominant. Since the reducing effect of the C
to CO_2 reaction is greater, the result is that less
carbon is needed per atomic unit of metal to be reduced.
In the case of carbon to carbon monoxide, each atomic
10   unit of carbon is oxidized from ground state zero to plus
2. Thus, for each atomic unit of metal ion (M) which is
being reduced by one oxidation state, one half atomic
unit of carbon is required. In the case of the carbon to
carbon dioxide reaction, one quarter atomic unit of
15   carbon is stoichiometrically required for each atomic
unit of metal ion (M) which is reduced by one oxidation
state, because carbon goes from ground state zero to a
plus 4 oxidation state. These same relationships apply
for each such metal ion being reduced and for each unit
20   reduction in oxidation state desired.

It is preferred to heat the starting materials
at a ramp rate of a fraction of a degree to 10°C per
minute and preferably about 2°C per minute. Once the
desired reaction temperature is attained, the reactants
25.   (starting materials) are held at the reaction temperature
for several hours. The heating is preferably conducted
under non-oxidizing or inert gas such as argon or vacuum.
Advantageously, a reducing atmosphere is not required,
although it may be used if desired. After reaction, the
30   products are preferably cooled from the elevated
temperature to ambient (room) temperature (i.e., 10°C to
40°C). Desirably, the cooling occurs at a rate similar
to the earlier ramp rate, and preferably 2°C/minute

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cooling. Such cooling rate has been found to be adequate
to achieve the desired structure of the final product.
It is also possible to quench the products at a cooling
rate on the order of about 100°C/minute. In some
5   instances, such rapid cooling (quench) may be preferred.

The present invention resolves the capacity
problem posed by widely used cathode active material. It
has been found that the capacity and capacity retention
of cells having the preferred active material of the
10   invention are improved over conventional materials.
Optimized cells containing lithium-mixed metal phosphates
of the invention potentially have performance improved
over commonly used lithium metal oxide compounds.
Advantageously, the new method of making the novel
15   lithium-mixed metal phosphate compounds of the invention
is relatively economical and readily adaptable to
commercial production.

Objects, features, and advantages of the
invention include an electrochemical cell or battery
20   based on lithium-mixed metal phosphates. Another object
is to provide an electrode active material which combines
the advantages of good discharge capacity and capacity
retention. It is also an object of the present invention
to provide electrodes which can be manufactured
25   economically. Another object is to provide a method for
forming electrode active material which lends itself to
commercial scale production for preparation of large
quantities.

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These and other objects, features, and
advantages will become apparent from the following
description of the preferred embodiments, claims, and
accompanying drawings.

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Brief Description of the Drawings

Figure 1 shows the results of an x-ray diffraction analysis, of the $LiFePO_4$ prepared according to the invention using $CuK\alpha$ radiation, $\lambda = 1.5405\text{Å}$. Bars

5   refer to simulated pattern from refined cell parameters, Space Group, SG = Pnma (62). The values are a = 10.2883Å (0.0020), b = 5.9759Å (0.0037), c = 4.6717Å (0.0012) 0.0072, cell volume = 287.2264Å^3 (0.0685). Density, p = 3.605 g/cc, zero = 0.452 (0.003). Peak at full width

10 half maximum, PFWHM = 0.21. Crystallite size from XRD data = 704Å.

Figure 2 is a voltage/capacity plot of $LiFePO_4$-containing cathode cycled with a lithium metal anode using constant current cycling at ± 0.2 milliamps per

15 square centimeter in a range of 2.5 to 4.0 volts at a temperature of about 23°C. The cathode contained 19.0mg of the $LiFePO_4$ active material, prepared by the method of the invention. The electrolyte comprised ethylene carbonate (EC) and dimethyl carbonate (DMC) in a weight

20 ratio of 2:1 and included a 1 molar concentration of $LiPF_6$ salt. The lithium-metal-phosphate containing electrode and the lithium metal counter electrode are maintained spaced apart by a glass fiber separator which is interpenetrated by the solvent and the salt.

25 Figure 3 shows multiple constant current cycling of $LiFePO_4$ active material cycled with a lithium metal anode using the electrolyte as described in connection with Figure 2 and cycled, charge and discharge at ± 0.2 milliamps per square centimeter, 2.5 to 4.0

30 volts at two different temperature conditions, 23°C and 60°C. Figure 3 shows the excellent rechargeability of

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the lithium iron phosphate/lithium metal cell, and also
shows the excellent cycling and specific capacity (mAh/g)
of the active material.

Figure 4 shows the results of an x-ray
5   diffraction analysis, of the $LiFe_{0.9}Mg_{0.1}PO_4$ prepared
according to the invention, using CuKα radiation, λ =
1.5405Å. Bars refer to simulated pattern from refined
cell parameters SG = Pnma (62). The values are a =
10.2688Å (0.0069), b = 5.9709Å (0.0072), c = 4.6762Å
10   (0.0054), cell volume = 286.7208Å (0.04294), p = 3.617
g/cc, zero = 0.702 (0.003), PFWHM = 0.01, and crystallite
= 950Å.

Figure 5 is a voltage/capacity plot of
$LiFe_{0.9}Mg_{0.1}PO_4$-containing cathode cycled with a lithium
15   metal anode using constant current cycling at ± 0.2
milliamps per square centimeter in a range of 2.5 to 4.0
volts. Other conditions are as described earlier with
respect to Figure 2. The cathode contained 18.9mg of the
$LiFe_{0.9}Mg_{0.1}PO_4$ active material prepared by the method of
20   the invention.

Figure 6 shows multiple constant current
cycling of $LiFe_{0.9}Mg_{0.1}PO_4$ cycled with a lithium metal
anode using the electrolyte as described in connection
with Figure 2 and cycled, charge and discharge at ± 0.2
25   milliamps per square centimeter, 2.5 to 4.0 volts at two
different temperature conditions, 23°C and 60°C. Figure
6 shows the excellent rechargeability of the lithium-
metal-phosphate/lithium metal cell, and also shows the
excellent cycling and capacity of the cell.

Figure 7 is a voltage/capacity plot of
$LiFe_{0.8}Mg_{0.2}PO_4$-containing cathode cycled with a lithium
metal anode using constant current cycling at ± 0.2
milliamps per square centimeter in a range of 2.5 to 4.0
volts at 23°C. Other conditions are as described earlier
with respect to **Figure 2**. The cathode contained 16mg of
the $LiFe_{0.8}Mg_{0.2}PO_4$ active material prepared by the method
of the invention.

Figure 8 shows the results of an x-ray
diffraction analysis, of the $LiFe_{0.9}Ca_{0.1}PO_4$ prepared
according to the invention, using CuKα radiation, λ =
1.5405Å. Bars refer to simulated pattern from refined
cell parameters SG = Pnma (62). The values are a =
10.3240Å (0.0045), b = 6.0042Å (0.0031), c = 4.6887Å
(0.0020), cell volume = 290.6370Å (0.1807), zero = 0.702
(0.003), p = 3.62 g/cc, PFWHM = 0.18, and crystallite =
680Å.

Figure 9 is a voltage/capacity plot of
$LiFe_{0.8}Ca_{0.2}PO_4$-containing cathode cycled with a lithium
metal anode using constant current cycling at ± 0.2
milliamps per square centimeter in a range of 2.5 to 4.0
volts at 23°. Other conditions are as described earlier
with respect to **Figure 2**. The cathode contained 18.5mg
of the $LiFe_{0.8}Ca_{0.2}PO_4$ active material prepared by the
method of the invention.

Figure 10 is a voltage/capacity plot of
$LiFe_{0.8}Zn_{0.2}PO_4$-containing cathode cycled with a lithium
metal anode using constant current cycling at ± 0.2
milliamps per square centimeter in a range of 2.5 to 4.0
volts at 23°C. Other conditions are as described earlier
with respect to **Figure 2**. The cathode contained 18.9mg

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of the $LiFe_{0.8}Zn_{0.2}PO_4$ active material prepared by the method of the invention.

Figure 11 shows the results of an x-ray diffraction analysis of the gamma-$Li_xV_2O_5$ (x = 1, gamma LiV_2O_5) prepared according to the invention using CuKα radiation λ = 1.5405Å. The values are a = 9.687Å (1), b = 3.603Å (2), and c = 10.677Å (3); phase type is gamma-$Li_xV_2O_5$ (x = 1); symmetry is orthorhombic; and space group is Pnma.

Figure 12 is a voltage/capacity plot of gamma-LiV_2O_5-containing cathode cycled with a lithium metal anode using constant current cycling at ± 0.2 milliamps per square centimeter in a range of 2.5 to 3.8 volts at 23°C. Other conditions are as described earlier with respect to Figure 2. The cathode contained 21mg of the gamma-LiV_2O_5 active material prepared by the method of the invention.

Figure 13 is a two-part graph based on multiple constant current cycling of gamma-LiV_2O_5 cycled with a lithium metal anode using the electrolyte as described in connection with Figure 2 and cycled, charge and discharge at ± 0.2 milliamps per square centimeter, 2.5 to 3.8 volts. In the two-part graph, Figure 13 shows the excellent rechargeability of the lithium-metal-oxide/lithium metal cell. Figure 13 shows the excellent cycling and capacity of the cell.

Figure 14 shows the results of an x-ray diffraction analysis of the $Li_3V_2(PO_4)_3$ prepared according to the invention. The analysis is based on CuKα

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radiation, $\lambda = 1.5405\text{Å}$. The values are a $= 12.184\text{Å}$ (2), b $= 8.679\text{Å}$ (2), c $= 8.627\text{Å}$ (3), and $\beta = 90.457°$ (4).

Figure 15 shows the results of an x-ray diffraction analysis of $Li_3V_2(PO_4)_3$ prepared according to a method described in U.S. Patent No. 5,871,866. The analysis is based on CuKα radiation, $\lambda = 1.5405\text{Å}$. The values are a $= 12.155\text{Å}$ (2), b $= 8.711\text{Å}$ (2), c $= 8.645\text{Å}$ (3); the angle beta is 90.175 (6); symmetry is Monoclinic; and space group is $P2_1/n$.

Figure 16 is an EVS (Electrochemical Voltage Spectroscopy) voltage/capacity profile for a cell with cathode material formed by the carbothermal reduction method of the invention. The cathode material is 13.8mg of $Li_3V_2(PO_4)_3$. The cell includes a lithium metal counter electrode in an electrolyte comprising ethylene carbonate (EC) and dimethyl carbonate (DMC) in a weight ratio of 2:1 and including a 1 molar concentration of $LiPF_6$ salt. The lithium-metal-phosphate containing electrode and the lithium metal counter electrode are maintained spaced apart by a fiberglass separator which is interpenetrated by the solvent and the salt. The conditions are ± 10 mV steps, between about 3.0 and 4.2 volts, and the critical limiting current density is less than or equal to 0.1 mA/cm^2.

Figure 17 is an EVS differential capacity versus voltage plot for the cell as described in connection with **Figure 16**.

Figure 18 shows multiple constant current cycling of $LiFe_{0.8}Mg_{0.2}PO_4$ cycled with a lithium metal anode using the electrolyte as described in connection

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with **Figure 2** and cycled, charge and discharge at ± 0.2 milliamps per square centimeter, 2.5 to 4.0 volts at two different temperature conditions, 23°C and 60°C. **Figure 18** shows the excellent rechargeability of the lithium-metal-phosphate/lithium metal cell, and also shows the excellent cycling and capacity of the cell.

Figure 19 is a graph of potential over time for the first four complete cycles of the $LiMg_{0.1}Fe_{0.9}PO_4$/MCMB graphite cell of the invention.

Figure 20 is a two-part graph based on multiple constant current cycling of $LiFe_{0.9}Mg_{0.1}PO_4$ cycled with an MCMB graphite anode using the electrolyte as described in connection with **Figure 2** and cycled, charge and discharge at ± 0.2 milliamps per square centimeter, 2.5 to 3.6 volts, 23°C and based on a C/10 (10 hour) rate. In the two-part graph, **Figure 20** shows the excellent rechargeability of the lithium-metal-phosphate/graphite cell. **Figure 20** shows the excellent cycling and capacity of the cell.

Figure 21 is a graph of potential over time for the first three complete cycles of the gamma-LiV_2O_5/MCMB graphite cell of the invention.

Figure 22 is a diagrammatic representation of a typical laminated lithium-ion battery cell structure.

Figure 23 is a diagrammatic representation of a typical multi-cell battery cell structure.

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Detailed Description of the Preferred Embodiments

The present invention provides lithium-mixed metal-phosphates, which are usable as electrode active materials, for lithium (Li^+) ion removal and insertion.

5   Upon extraction of the lithium ions from the lithium-mixed-metal-phosphates, significant capacity is achieved. In one aspect of the invention, electrochemical energy is provided when combined with a suitable counter electrode by extraction of a quantity x of lithium from lithium-

10   mixed-metal-phosphates $Li_{a-x}MI_bMII_c(PO_4)_d$. When a quantity x of lithium is removed per formula unit of the lithium-mixed-metal phosphate, metal MI is oxidized. In another aspect, metal MII is also oxidized. Therefore, at least one of MI and MII is oxidizable from its initial

15   condition in the phosphate compound as Li is removed. Consider the following which illustrate the mixed metal compounds of the invention: $LiFe_{1-y}Sn_yPO_4$, has two oxidizable elements, Fe and Sn; in contrast, $LiFe_{1-y}Mg_yPO_4$ has one oxidizable metal, the metal Fe.

20   In another aspect, the invention provides a lithium ion battery which comprises an electrolyte; a negative electrode having an insertion active material; and a positive electrode comprising a lithium-mixed-metal-phosphate active material characterized by an

25   ability to release lithium ions for insertion into the negative electrode active material. The lithium-mixed-metal-phosphate is desirably represented by the nominal general formula $Li_aMI_bMII_c(PO_4)_d$. Although the metals MI and MII may be the same, it is preferred that the metals

30   MI and MII are different. Desirably, in the phosphate compound MI is a metal selected from the group: Fe, Co, Ni, Mn, Cu, V, Sn, Ti, Cr and mixtures thereof, and MI is

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most desirably a transition metal or mixture thereof
selected from said group. Most preferably, MI has a +2
valence or oxidation state.

    In another aspect, MII is selected from Mg, Ca,
5   Zn, Sr, Pb, Cd, Sn, Ba, Be, and mixtures thereof. Most
preferably, MII has a +2 valence or oxidation state. The
lithium-mixed-metal-phosphate is preferably a compound
represented by the nominal general formula
$Li_{a-x}MI_bMII_c(PO_4)_d$, signifying the preferred composition
10   and its capability to release x lithium. Accordingly,
during cycling, charge and discharge, the value of x
varies as x greater than or equal to 0 and less than or
equal to a. The present invention resolves a capacity
problem posed by conventional cathode active materials.
15   Such problems with conventional active materials are
described by Tarascon in U.S. Patent No. 5,425,932, using
$LiMn_2O_4$ as an example. Similar problems are observed
with $LiCoO_2$, $LiNiO_2$, and many, if not all, lithium metal
chalcogenide materials. The present invention
20   demonstrates that significant capacity of the cathode
active material is utilizable and maintained.

    A preferred novel procedure for forming the
lithium-mixed-metal-phosphate $Li_aMI_bMII_c(PO_4)_d$ compound
active material will now be described. In addition, the
25   preferred novel procedure is also applicable to formation
of other lithium metal compounds, and will be described
as such. The basic procedure will be described with
reference to exemplary starting materials but is not
limited thereby. The basic process comprises conducting
30   a reaction between a lithium compound, preferably lithium
carbonate (Li_2CO_3), metal compound(s), for example,
vanadium pentoxide (V_2O_5), iron oxide (Fe_2O_3), and/or

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manganese hydroxide, and a phosphoric acid derivative,
preferably the phosphoric acid ammonium salt, diammonium
hydrogen phosphate, $(NH_4)_2H(PO_4)$. Each of the precursor
starting materials are available from a number of
5   chemical outfits including Aldrich Chemical Company and
Fluka. Using the method described herein, $LiFePO_4$ and
$LiFe_{0.9}Mg_{0.1}PO_4$, $Li_3V_2(PO_4)_3$ were prepared with approximately
a stoichiometric amount of Li_2CO_3, the respective metal
compound, and $(NH_4)_2HPO_4$. Carbon powder was included with
10 these precursor materials. The precursor materials were
initially intimately mixed and dry ground for about 30
minutes. The intimately mixed compounds were then
pressed into pellets. Reaction was conducted by heating
in an oven at a preferred ramped heating rate to an
15 elevated temperature, and held at such elevated
temperature for several hours to complete formation of
the reaction product. The entire reaction was conducted
in a non-oxidizing atmosphere, under flowing pure argon
gas. The flow rate will depend upon the size of the oven
20 and the quantity needed to maintain the atmosphere. The
oven was permitted to cool down at the end of the
reaction period, where cooling occurred at a desired rate
under argon. Exemplary and preferred ramp rates,
elevated reaction temperatures and reaction times are
25 described herein. In one aspect, a ramp rate of
2°/minute to an elevated temperature in a range of 750°C
to 800°C was suitable along with a dwell (reaction time)
of 8 hours. Refer to Reactions 1, 2, 3 and 4 herein. In
another variation per Reaction 5, a reaction temperature
30 of 600°C was used along with a dwell time of about one
hour. In still another variation, as per Reaction 6, a
two-stage heating was conducted, first to a temperature
of 300°C and then to a temperature of 850°.

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The general aspects of the above synthesis
route are applicable to a variety of starting materials.
Lithium-containing compounds include Li_2O (lithium
oxide), LiH_2PO_4 (lithium hydrogen phosphate),
5      $Li_2C_2O_4$ (lithium oxalate), LiOH (lithium hydroxide),
$LiOH.H_2O$ (lithium hydroxide monohydride), and $LiHCO_3$
(lithium hydrogen carbonate). The metal compounds(s) are
reduced in the presence of the reducing agent, carbon.
The same considerations apply to other lithium-metal- and
10   phosphate-containing precursors. The thermodynamic
considerations such as ease of reduction, of the selected
precursors, the reaction kinetics, and the melting point
of the salts will cause adjustment in the general
procedure, such as, amount of carbon reducing agent, and
15   the temperature of reaction.

       Figures 1 through **21** which will be described
more particularly below show characterization data and
capacity in actual use for the cathode materials
(positive electrodes) of the invention. Some tests were
20   conducted in a cell comprising a lithium metal counter
electrode (negative electrode) and other tests were
conducted in cells having a carbonaceous counter
electrode. All of the cells had an $EC:DMC-LiPF_6$
electrolyte.

25   Typical cell configurations will now be
described with reference to **Figures 22 and 23;** and such
battery or cell utilizes the novel active material of the
invention. Note that the preferred cell arrangement
described here is illustrative and the invention is not
30   limited thereby. Experiments are often performed, based
on full and half cell arrangements, as per the following
description. For test purposes, test cells are often

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fabricated using lithium metal electrodes. When forming
cells for use as batteries, it is preferred to use an
insertion positive electrode as per the invention and a
graphitic carbon negative electrode.

5   A typical laminated battery cell structure 10
is depicted in **Figure 22**. It comprises a negative
electrode side 12, a positive electrode side 14, and an
electrolyte/separator 16 there between. Negative
electrode side 12 includes current collector 18, and
10   positive electrode side 14 includes current collector 22.
A copper collector foil 18, preferably in the form of an
open mesh grid, upon which is laid a negative electrode
membrane 20 comprising an insertion material such as
carbon or graphite or low-voltage lithium insertion
15   compound, dispersed in a polymeric binder matrix. An
electrolyte/separator film 16 membrane is preferably a
plasticized copolymer. This electrolyte/separator
preferably comprises a polymeric separator and a suitable
electrolyte for ion transport. The electrolyte/separator
20   is positioned upon the electrode element and is covered
with a positive electrode membrane 24 comprising a
composition of a finely divided lithium insertion
compound in a polymeric binder matrix. An aluminum
collector foil or grid 22 completes the assembly.
25   Protective bagging material 40 covers the cell and
prevents infiltration of air and moisture.

          In another embodiment, a multi-cell battery
configuration as per **Figure 23** is prepared with copper
current collector 51, negative electrode 53,
30   electrolyte/separator 55, positive electrode 57, and
aluminum current collector 59. Tabs 52 and 58 of the
current collector elements form respective terminals for

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the battery structure. As used herein, the terms "cell"
and "battery" refer to an individual cell comprising
anode/electrolyte/cathode and also refer to a multi-cell
arrangement in a stack.

5   The relative weight proportions of the
components of the positive electrode are generally: 50-
90% by weight active material; 5-30% carbon black as the
electric conductive diluent; and 3-20% binder chosen to
hold all particulate materials in contact with one
10   another without degrading ionic conductivity. Stated
ranges are not critical, and the amount of active
material in an electrode may range from 25-95 weight
percent. The negative electrode comprises about 50-95%
by weight of a preferred graphite, with the balance
15   constituted by the binder. A typical electrolyte
separator film comprises approximately two parts polymer
for every one part of a preferred fumed silica. The
conductive solvent comprises any number of suitable
solvents and salts. Desirable solvents and salts are
20   described in U.S. Patent Nos. 5,643,695 and 5,418,091.
One example is a mixture of EC:DMC:LiPF$_6$ in a weight
ratio of about 60:30:10.

             Solvents are selected to be used individually
or in mixtures, and include dimethyl carbonate (DMC),
25   diethylcarbonate (DEC), dipropylcarbonate (DPC),
ethylmethylcarbonate (EMC), ethylene carbonate (EC),
propylene carbonate (PC), butylene carbonate, lactones,
esters, glymes, sulfoxides, sulfolanes, etc. The
preferred solvents are EC/DMC, EC/DEC, EC/DPC and EC/EMC.
30   The salt content ranges from 5% to 65% by weight,
preferably from 8% to 35% by weight.

Those skilled in the art will understand that
any number of methods are used to form films from the
casting solution using conventional meter bar or doctor
blade apparatus. It is usually sufficient to air-dry the

5   films at moderate temperature to yield self-supporting
films of copolymer composition. Lamination of assembled
cell structures is accomplished by conventional means by
pressing between metal plates at a temperature of about
120-160°C. Subsequent to lamination, the battery cell

10   material may be stored either with the retained
plasticizer or as a dry sheet after extraction of the
plasticizer with a selective low-boiling point solvent.
The plasticizer extraction solvent is not critical, and
methanol or ether are often used.

15   Separator membrane element 16 is generally
polymeric and prepared from a composition comprising a
copolymer. A preferred composition is the 75 to 92%
vinylidene fluoride with 8 to 25% hexafluoropropylene
copolymer (available commercially from Atochem North

20   America as Kynar FLEX) and an organic solvent
plasticizer. Such a copolymer composition is also
preferred for the preparation of the electrode membrane
elements, since subsequent laminate interface
compatibility is ensured. The plasticizing solvent may

25   be one of the various organic compounds commonly used as
solvents for electrolyte salts, e.g., propylene carbonate
or ethylene carbonate, as well as mixtures of these
compounds. Higher-boiling plasticizer compounds such as
dibutyl phthalate, dimethyl phthalate, diethyl phthalate,

30   and tris butoxyethyl phosphate are particularly suitable.
Inorganic filler adjuncts, such as fumed alumina or
silanized fumed silica, may be used to enhance the
physical strength and melt viscosity of a separator

membrane and, in some compositions, to increase the
subsequent level of electrolyte solution absorption.

In the construction of a lithium-ion battery, a
current collector layer of aluminum foil or grid is
5   overlaid with a positive electrode film, or membrane,
separately prepared as a coated layer of a dispersion of
insertion electrode composition. This is typically an
insertion compound such as $LiMn_2O_4$ (LMO), $LiCoO_2$, or
$LiNiO_2$, powder in a copolymer matrix solution, which is
10   dried to form the positive electrode. An
electrolyte/separator membrane is formed as a dried
coating of a composition comprising a solution containing
VdF:HFP copolymer and a plasticizer solvent is then
overlaid on the positive electrode film. A negative
15   electrode membrane formed as a dried coating of a
powdered carbon or other negative electrode material
dispersion in a VdF:HFP copolymer matrix solution is
similarly overlaid on the separator membrane layer. A
copper current collector foil or grid is laid upon the
20   negative electrode layer to complete the cell assembly.
Therefore, the VdF:HFP copolymer composition is used as a
binder in all of the major cell components, positive
electrode film, negative electrode film, and
electrolyte/separator membrane. The assembled components
25   are then heated under pressure to achieve heat-fusion
bonding between the plasticized copolymer matrix
electrode and electrolyte components, and to the
collector grids, to thereby form an effective laminate of
cell elements. This produces an essentially unitary and
30   flexible battery cell structure.

Examples of forming cells containing metallic
lithium anode, insertion electrodes, solid electrolytes

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and liquid electrolytes can be found in U.S. Patent Nos.
4,668,595; 4,830,939; 4,935,317; 4,990,413; 4,792,504;
5,037,712; 5,262,253; 5,300,373; 5,435,054; 5,463,179;
5,399,447; 5,482,795 and 5,411,820; each of which is

5   incorporated herein by reference in its entirety. Note
that the older generation of cells contained organic
polymeric and inorganic electrolyte matrix materials,
with the polymeric being most preferred. The
polyethylene oxide of 5,411,820 is an example. More

10   modern examples are the VdF:HFP polymeric matrix.
Examples of casting, lamination and formation of cells
using VdF:HFP are as described in U.S. Patent Nos.
5,418,091; 5,460,904; 5,456,000; and 5,540,741; assigned
to Bell Communications Research, each of which is

15   incorporated herein by reference in its entirety.

          As described earlier, the electrochemical cell
operated as per the invention, may be prepared in a
variety of ways. In one embodiment, the negative
electrode may be metallic lithium. In more desirable

20   embodiments, the negative electrode is an insertion
active material, such as, metal oxides and graphite.
When a metal oxide active material is used, the
components of the electrode are the metal oxide,
electrically conductive carbon, and binder, in

25   proportions similar to that described above for the
positive electrode. In a preferred embodiment, the
negative electrode active material is graphite particles.
For test purposes, test cells are often fabricated using
lithium metal electrodes. When forming cells for use as

30   batteries, it is preferred to use an insertion metal
oxide positive electrode and a graphitic carbon negative
electrode. Various methods for fabricating
electrochemical cells and batteries and for forming

electrode components are described herein. The invention is not, however, limited by any particular fabrication method.

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Formation of Active Materials

EXAMPLE I

Reaction 1(a). $LiFePO_4$ formed from $FePO_4$

$$FePO_4 + 0.5\ Li_2CO_3 + 0.5\ C \rightarrow LiFePO_4 + 0.5\ CO_2 + 0.5\ CO$$
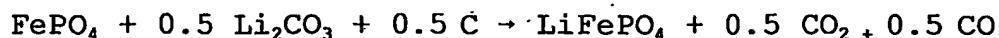
5   (a)   Pre-mix reactants in the following proportions
            using ball mill. Thus,

                  1 mol $FePO_4$ 150.82g
                  0.5 mol Li_2CO_3 36.95g
                  0.5 mol carbon   6.0g

10   (but use <u>100%</u> excess carbon → 12.00g)

      (b)   Pelletize powder mixture

      (c)   Heat pellet to 750°C at a rate of 2°/minute in
            flowing inert atmosphere (e.g. argon). Dwell
            for 8 hours at 750°C under argon.

15   (d)   Cool to room temperature at 2°/minute under
            argon.

      (e)   Powderize pellet.

            Note that at 750°C this is predominantly a CO
            reaction. This reaction is able to be
20   conducted at a temperature in a range of about
            700°C to about 950°C in argon as shown, and
            also under other inert atmospheres such as
            nitrogen or vacuum.

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EXAMPLE II

Reaction 1(b). $LiFePO_4$ formed from Fe_2O_3

$0.5\ Fe_2O_3 + 0.5\ Li_2CO_3 + (NH_4)_2HPO_4 + 0.5\ C \rightarrow LiFePO_4 +$
$0.5\ CO_2 + 2\ NH_3 + 3/2\ H_2O + 0.5\ CO$
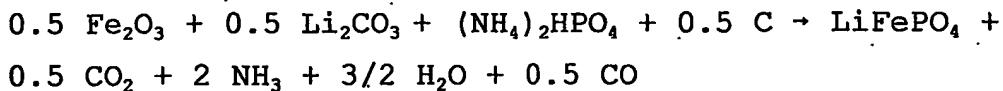
5   (a)   Premix powders in the following proportions

0.5 mol Fe_2O_3	79.85g
0.5 mol Li_2CO_3	36.95g
1 mol $(NH_4)_2HPO_4$	132.06g
0.5 mol carbon	6.00g

10   (use 100% excess carbon → 12.00g)

       (b)   Pelletize powder mixture

   (c)   Heat pellet to 750°C at a rate of 2°/minute in
             flowing inert atmosphere (e.g. argon). Dwell
             for 8 hours at 750°C under argon.

15   (d)   Cool to room temperature at 2°/minute under
             argon.

       (e)   Powderize

EXAMPLE III

Reaction 1(c). $LiFePO_4$ – from $Fe_3(PO_4)_2$

20   Two steps:

Part I.   Carbothermal preparation of $Fe_3(PO_4)_2$

$3/2\ Fe_2O_3\ +\ 2\,(NH_4)_2HPO_4\ +\ 3/2\ C\ \rightarrow\ Fe_3(PO_4)_2\ +$

$3/2\ CO\ +\ 4NH_3\ +\ 5/2\ H_2O$
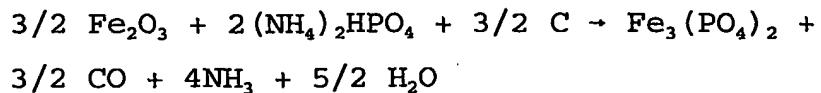
   (a) Premix reactants in the following proportions

       $3/2$ mol Fe_2O_3 239.54g

       2 mol $(NH_4)_2HPO_4$ 264.12g

       $3/2$ mol carbon   18.00g

   (use 100% excess carbon → 36.00g)

   (b) Pelletize powder mixture

   (c) Heat pellet to 800°C at a rate of 2°/minute in
        flowing inert atmosphere (e.g. argon). Dwell
        for 8 hours at 750°C under argon.

   (d) Cool to room temperature at 2°C/minute under
        argon.

   (e) Powderize pellet.

Part II.   Preparation of $LiFePO_4$ from the $Fe_3(PO_4)_2$ of
           Part I.

$Li_3PO_4\ +\ Fe_3(PO_4)_2\ \rightarrow\ 3\ LiFePO_4$

   (a) Premix reactants in the following proportions

       1 mol Li_3PO_4 115.79g

       1 mol $Fe_3(PO_4)_2$ 357.48g

   (b) Pelletize powder mixture

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(c) Heat pellet to 750°C at a rate of 2°/minute in
flowing inert atmosphere (e.g. argon). Dwell
for 8 hours at 750°C under argon.

(d) Cool to room temperature at 2°C/minute under
5   argon.

(e) Powderize pellet.

EXAMPLE IV

Reaction 2(a). $LiFe_{0.9}Mg_{0.1}PO_4$ ($LiFe_{1-y}Mg_yPO_4$) formed from
$FePO_4$

10       $0.5 Li_2CO_3 + 0.9 FePO_4 + 0.1 Mg(OH)_2 + 0.1(NH_4)_2HPO_4 +$
$0.45C \rightarrow LiFe_{0.9}Mg_{0.1}PO_4 + 0.5CO_2 + 0.45CO + 0.2NH_3 +$
$0.25 H_2O$
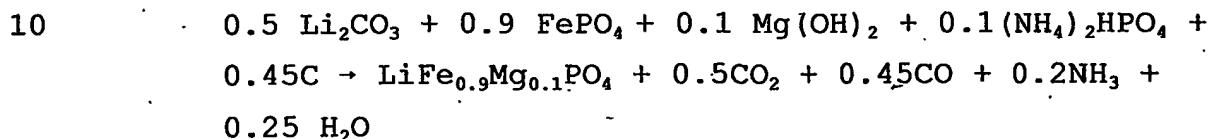
(a) Pre-mix reactants in the following proportions

0.50 mol Li_2CO_3	=	36.95g
0.90 mol $FePO_4$	=	135.74g
0.10 mol $Mg(OH)_2$	=	5.83g
0.10 mol $(NH_4)_2HPO_4$	=	1.32g
0.45 mol carbon	=	5.40g

(use 100% excess carbon → 10.80g)

20   (b) Pelletize powder mixture

(c) Heat to 750°C at a rate of 2°/minute in argon.
Hold for 8 hours dwell at 750°C in argon

(d) Cool at a rate of 2°/minute

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(e)   Powderize pellet.

EXAMPLE V

Reaction 2(b). $LiFe_{0.9}Mg_{0.1}PO4$ ($LiFe_{1-y}Mg_yPO_4$) formed from

5   Fe_2O_3

$0.50\ Li_2CO_3 + 0.45\ Fe_2O_3 + 0.10\ Mg(OH)_2 + (NH_4)_2HPO_4 +$
$0.45C \rightarrow\ LiFe_{0.9}Mg_{0.1}PO_4 + 0.5\ CO_2 + 0.45\ CO + 2\ NH_3 +$
$1.6\ H_2O$
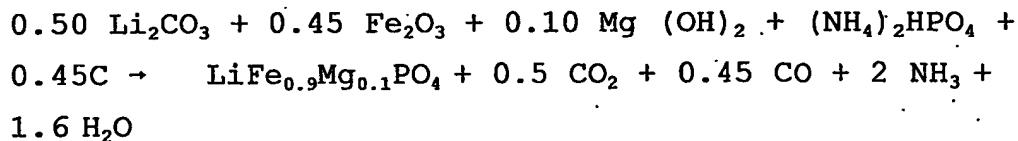
10   (a)   Pre-mix reactants in following ratio

0.50 mol Li_2CO_3	=	36.95g
0.45 mol Fe_2O_3	=	71.86g
0.10 mol $Mg(OH)_2$	=	5.83g
1.00 mol $(NH_4)_2HPO_4$	=	132.06g
0.45 mol carbon	=	5.40g

15

(use 100% excess carbon → 10.80g)

(b)   Pelletize powder mixture

(c)   Heat to 750°C at a rate of 2°/minute in argon.
      Hold for 8 hours dwell at 750°C in argon

20   (d)   Cool at a rate of 2°/minute

(e)   Powderize pellet.

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EXAMPLE VI

Reaction 2(c). $LiFe_{0.9}Mg_{0.1}PO_4$ ($LiFe_{1-y}Mg_yPO_4$) formed from LiH_2PO_4

5        $1.0\ LiH_2PO_4 + 0.45\ Fe_2O_3 + 0.10\ Mg(OH)_2 + 0.45C \rightarrow$

$LiFe_{0.9}Mg_{0.1}PO_4 + 0.45\ CO + 1.1\ H_2O$
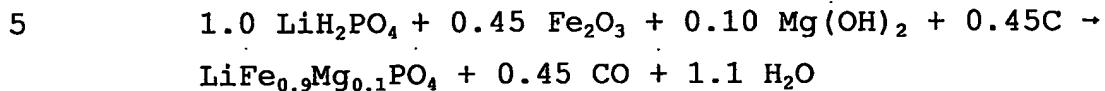
   (a)   Pre-mix reactants in the following proportions

1.00 mol LiH_2PO_4	=	103.93g
0.45 mol Fe_2O_3	=	71.86g
0.10 mol $Mg(OH)_2$	=	5.83g
0.45 mol carbon	=	5.40g

10

   (use 100% excess carbon → 10.80g)

   (b)   Pelletize powder mixture

15   (c)   Heat to 750°C at a rate of 2°/minute in argon.
         Hold for 8 hours dwell at 750°C in argon

   (d)   Cool at a rate of 2°/minute

   (e)   Powderize pellet.

EXAMPLE VII

20   Reaction 3.   Formation of $LiFe_{0.9}Ca_{0.1}PO_4$
      ($LiFe_{1-y}Ca_yPO_4$) from Fe_2O_3
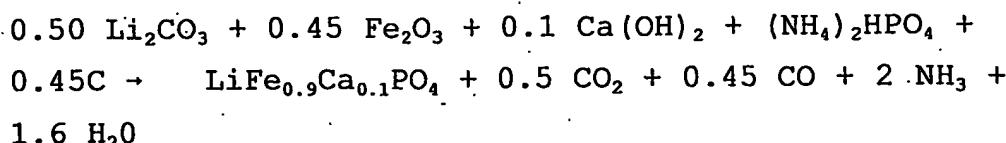
      $0.50\ Li_2CO_3 + 0.45\ Fe_2O_3 + 0.1\ Ca(OH)_2 + (NH_4)_2HPO_4 +$

      $0.45C \rightarrow\ LiFe_{0.9}Ca_{0.1}PO_4 + 0.5\ CO_2 + 0.45\ CO + 2\ NH_3 +$

      $1.6\ H_2O$

(a)   Pre-mix reactants in the following proportions

$$0.50 \text{ mol } Li_2CO_3 \qquad = \qquad 36.95g$$

$$0.45 \text{ mol } Fe_2O_3 \qquad = \qquad 71.86g$$

$$0.10 \text{ mol } Ca(OH)_2 \qquad = \qquad 7.41g$$

5
$$1.00 \text{ mol } (NH_4)_2HPO_4 \qquad = \qquad 132.06g$$

$$0.45 \text{ mol carbon} \qquad = \qquad 5.40g$$

(100% excess carbon → 10.80g)

(b)   Pelletize powder mixture

10   (c)   Heat to 750°C at a rate of 2°/minute in argon.
              Hold for 8 hours dwell at 750°C in argon

(d)   Cool at a rate of 2°/minute

(e)   Powderize pellet.

EXAMPLE VIII

15   Reaction 4.   Formation of $LiFe_{0.9}Zn_{0.1}PO_4$

                     $(LiFe_{1-y}Zn_yPO_4)$ from Fe_2O_3.

$$0.50 \ Li_2CO_3 + 0.45 \ Fe_2O_3 + 0.033 \ Zn_3(PO_4)_2 +$$

$$0.933 (NH_4)_2HPO_4 + 0.45 \ C \rightarrow LiFe_{0.9}Zn_{0.1}PO_4 + 0.50 \ CO_2 +$$

$$0.45 \ CO + 1.866 \ NH_3 + 1.2 \ H_2O$$
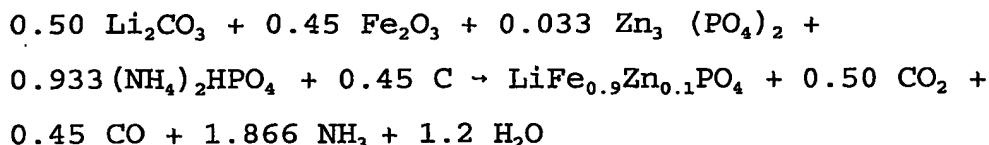
20   Pre-mix reactants in the following proportions

$$0.50 \text{ mol } Li_2CO_3 \qquad = \qquad 36.95g$$

$$0.45 \text{ mol } Fe_2O_3 \qquad = \qquad 71.86g$$

$$0.033 \text{ mol } Zn_3(PO_4)_2 \qquad = \qquad 12.74g$$

$$0.933 \text{ mol } (NH_4)_2HPO_4 \qquad = \qquad 123.21g$$

40

$$0.45 \text{ mol carbon} \quad = \quad 5.40g$$

(100% excess carbon → 10.80g)

(b)   Pelletize powder mixture

(c)   Heat to 750°C at a rate of 2°/minute in argon.
       Hold for 8 hours dwell at 750°C in argon

(d)   Cool at a rate of 2°/minute

(e)   Powderize pellet.

EXAMPLE IX

Reaction 5.   Formation of gamma-LiV_2O_5 (γ)

$$V_2O_5 + 0.5 \ Li_2CO_3 + 0.25 \ C \rightarrow LiV_2O_5 + 3/4 \ CO_2$$
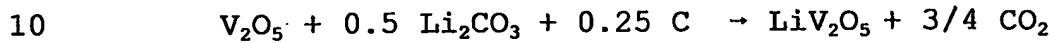
(a)   Pre-mix alpha V_2O_5, Li_2CO_3 and Shiwinigan Black
       (carbon) using ball mix with suitable media.
       Use a 25% weight excess of carbon over the
       reaction amounts above. For example, according
       to reaction above:

Need: 1 mol V_2O_5 181.88g
           0.5 mol Li_2CO_3 36.95g
           0.25 mol carbon   3.00g

(but use 25% excess carbon → 3.75g)

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    (b)   Pelletize powder mixture

    (c)   Heat pellet to 600°C in flowing argon (or other inert atmosphere) at a heat rate of approximately 2°/minute. Hold at 600°C for about 60 minutes.

    (d)   Allow to cool to room temperature in argon at cooling rate of about 2°/minute.

    (e)   Powderize pellet using mortar and pestle

This reaction is able to be conducted at a temperature in a range of about 400°C to about 650°C in argon as shown, and also under other inert atmospheres such as nitrogen or vacuum. This reaction at this temperature range is primarily $C \rightarrow CO_2$. Note that the reaction $C \rightarrow CO$ primarily occurs at a temperature over about 650°C (HT, high temperature); and the reaction $C \rightarrow CO_2$ primarily occurs at a temperature of under about 650°C (LT, low temperature). The reference to about 650°C is approximate and the designation "primarily" refers to the predominant reaction thermodynamically favored although the alternate reaction may occur to some extent.

EXAMPLE X

Reaction 6.   Formation of $Li_3V_2(PO_4)_3$

$$V_2O_5 + 3/2\ Li_2CO_3 + 3(NH_4)_2HPO_4 + C \rightarrow Li_3V_2(PO_4)_3 + 2\ CO + 3/2\ CO_2 + 6\ NH_3 + 9/2\ H_2O$$

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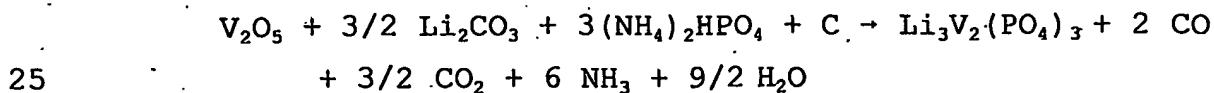
(a)   Pre-mix reactants above using ball mill with
       suitable media. Use a 25% weight excess of
       carbon. Thus,

                     1 mol V$_2$O$_5$ 181.88g
5   3/2 mol Li$_2$CO$_3$ 110.84g
                     3 mol (NH$_4$)$_2$HPO$_4$ 396.18g
                     1 mol carbon   12.01g

              (but use 25% excess carbon → 15.01g)

(b)   Pelletize powder mixture

10   (c)   Heat pellet at 2°/minute to 300°C to remove CO$_2$
             (from Li$_2$CO$_3$) and to remove NH$_3$, H$_2$O. Heat in
             an inert atmosphere (e.g. argon). Cool to room
             temperature.

(d)   Powderize and repelletize

15   (e)   Heat pellet in inert atmosphere at a rate of
             2°C/minute to 850°C. Dwell for 8 hours at
             850°C

(f)   Cool to room temperature at a rate of 2°/minute
       in argon.

20   (e)   Powderize

           This reaction is able to be conducted at a
    temperature in a range of about 700°C to about 950°C in
    argon as shown, and also under other inert atmospheres
    such as nitrogen or vacuum. A reaction temperature
25   greater than about 670°C ensures C → CO reaction is
    primarily carried out.

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Characterization of Active Materials
and Formation and Testing of Cells

Referring to **Figure 1**, the final product
$LiFePO_4$, prepared from Fe_2O_3 metal compound per Reaction
5   1(b), appeared brown/black in color. This olivine
material product included carbon that remained after
reaction. Its $CuK\alpha$ x-ray diffraction pattern contained
all of the peaks expected for this material as shown in
Figure 1. The pattern evident in **Figure 1** is consistent
10   with the single phase olivine phosphate, $LiFePO_4$. This
is evidenced by the position of the peaks in terms of the
scattering angle 2 θ (theta), x axis. The x-ray pattern
showed no peaks due to the presence of precursor oxides
indicating that the solid state reaction is essentially
15   entirely completed. Here the space group SG = pnma (62)
and the lattice parameters from XRD refinement are
consistent with the olivine structure. The values are a
= 10.2883Å (0.0020), b = 5.9759 (0.0037), c = 4.6717Å
(0.0012) 0.0072, cell volume = 287.2264Å^3 (0.0685).
20   Density, p = 3.605 g/cc, zero = 0.452 (0.003). Peak at
full width half maximum, PFWHM = 0.21. Crystallite size
from XRD data = 704Å.

The x-ray pattern demonstrates that the product
of the invention was indeed the nominal formula $LiFePO_4$.
25   The term "nominal formula" refers to the fact that the
relative proportion of atomic species may vary slightly
on the order of 2 percent to 5 percent, or more
typically, 1 percent to 3 percent, and that some portion
of P may be substituted by Si, S or As; and some portion
30   of O may be substituted by halogen, preferably F.

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The LiFePO$_4$, prepared as described immediately above, was tested in an electrochemical cell. The positive electrode was prepared as described above, using 19.0mg of active material. The positive electrode

5   contained, on a weight % basis, 85% active material, 10% carbon black, and 5% EPDM. The negative electrode was metallic lithium. The electrolyte was a 2:1 weight ratio mixture of ethylene carbonate and dimethyl carbonate within which was dissolved 1 molar LiPF$_6$. The cells were

10   cycled between about 2.5 and about 4.0 volts with performance as shown in **Figures 2 and 3.**

Figure 2 shows the results of the first constant current cycling at 0.2 milliamps per square centimeter between about 2.5 and 4.0 volts based upon

15   about 19 milligrams of the LiFePO$_4$ active material in the cathode (positive electrode). In an as prepared, as assembled, initial condition, the positive electrode active material is LiFePO$_4$. The lithium is extracted from the LiFePO$_4$ during charging of the cell. When fully

20   charged, about 0.72 unit of lithium had been removed per formula unit. Consequently, the positive electrode active material corresponds to Li$_{1-x}$FePO$_4$ where x appears to be equal to about 0.72, when the cathode material is at 4.0 volts versus Li/Li$^+$. The extraction represents

25   approximately 123 milliamp hours per gram corresponding to about 2.3 milliamp hours based on 19 milligrams active material. Next, the cell is discharged whereupon a quantity of lithium is re-inserted into the LiFePO$_4$. The re-insertion corresponds to approximately 121 milliamp

30   hours per gram proportional to the insertion of essentially all of the lithium. The bottom of the curve corresponds to approximately 2.5 volts. The total

45

cumulative capacity demonstrated during the entire
extraction-insertion cycle is 244mAh/g.

Figure 3 presents data obtained by multiple
constant current cycling at 0.2 milliamp hours per square
5   centimeter of the $LiFePO_4$ versus lithium metal counter
electrode between 2.5 and 4.0 volts. Data is shown for
two temperatures, 23°C and 60°C. **Figure 3** shows the
excellent rechargeability of the $LiFePO_4$ cell, and also
shows good cycling and capacity of the cell. The
10   performance shown after about 190 to 200 cycles is good
and shows that electrode formulation is very desirable.

Referring to **Figure 4**, there is shown data for
the final product $LiFe_{0.9}Mg_{0.1}PO_4$, prepared from the metal
compounds Fe_2O_3 and $Mg(OH)_2 \rightarrow Mg(OH)_2$, per Reaction 2(b).
15   Its CuKα x-ray diffraction pattern contained all of the
peaks expected for this material as shown in **Figure 4.**
The pattern evident in **Figure 4** is consistent with the
single phase olivine phosphate compound, $LiFe_{0.9}Mg_{0.1}PO_4$.
This is evidenced by the position of the peaks in terms
20   of the scattering angle 2 θ (theta), x axis. The x-ray
pattern showed no peaks due to the presence of precursor
oxides indicating that the solid state reaction is
essentially entirely completed. Here the space group SG
= Pnma (62) and the lattice parameters from XRD
25   refinement are consistent with the olivine structure.
The values are a = 10.2688Å (0.0069), b = 5.9709Å
(0.0072), c = 4.6762Å (0.0054), cell volume = 286.7208Å
(0.04294), p = 3.617 g/cc, zero = 0.702 (0.003), PFWHM =
0.01, and crystallite = 950Å.

30   The x-ray pattern demonstrates that the product
of the invention was indeed the nominal formula

$LiFe_{0.9}Mg_{0.1}PO_4$. The term "nominal formula" refers to the fact that the relative proportion of atomic species may vary slightly on the order of 2 percent to 5 percent, or more typically, 1 percent to 3 percent, and that some
5   substitution of P and O may be made while maintaining the basic olivine structure.

       The $LiFe_{0.9}Mg_{0.1}PO_4$, prepared as described immediately above, was tested in an electrochemical cell. The positive electrode was prepared as described above,
10   using 18.9mg of active materials. The positive electrode, negative electrode and electrolyte were prepared as described earlier and in connection with **Figure 1**. The cell was between about 2.5 and about 4.0 volts with performance as shown in **Figures 4, 5 and 6**.

15   **Figure 5** shows the results of the first constant current cycling at 0.2 milliamps per square centimeter between about 2.5 and 4.0 volts based upon about 18.9 milligrams of the $LiFe_{0.9}Mg_{0.1}PO_4$ active material in the cathode (positive electrode). In an as
20   prepared, as assembled, initial condition, the positive electrode active material is $LiFe_{0.9}Mg_{0.1}PO_4$. The lithium is extracted from the $LiFe_{0.9}Mg_{0.1}PO_4$ during charging of the cell. When fully charged, about 0.87 units of lithium have been removed per formula unit.
25   Consequently, the positive electrode active material corresponds to $Li_{1-x}Fe_{0.9}Mg_{0.1}PO_4$ where x appears to be equal to about 0.87, when the cathode material is at 4.0 volts versus Li/Li^+. The extraction represents approximately 150 milliamp hours per gram corresponding to about 2.8
30   milliamp hours based on 18.9 milligrams active material. Next, the cell is discharged whereupon a quantity of lithium is re-inserted into the $LiFe_{0.9}Mg_{0.1}PO_4$. The re-

insertion corresponds to approximately 146 milliamp hours
per gram proportional to the insertion of essentially all
of the lithium. The bottom of the curve corresponds to
approximately 2.5 volts. The total cumulative specific
5   capacity over the entire cycle is 296 mAhr/g. This
material has a much better cycle profile than the
LiFePO$_4$. **Figure 5** (LiFe$_{0.9}$Mg$_{0.1}$PO$_4$) shows a very well
defined and sharp peak at about 150 mAh/g. In contrast,
Figure 2 (LiFePO$_4$) shows a very shallow slope leading to
10   the peak at about 123 mAh/g. The Fe-phosphate **(Figure 2)**
provides 123 mAh/g compared to its theoretical capacity
of 170 mAh/g. This ratio of 123/170, 72% is relatively
poor compared to the Fe/Mg-phosphate. The Fe/Mg-
phosphate **(Figure 5)** provides 150 mAh/g compared to a
15   theoretical capacity of 160, a ratio of 150/160 or 94%.

Figure 6 presents data obtained by multiple
constant current cycling at 0.2 milliamp hours per square
centimeter of the LiFe$_{0.9}$Mg$_{0.1}$PO$_4$ versus lithium metal
counter electrode between 2.5 and 4.0 volts. **Figure 6**
20   shows the excellent rechargeability of the
Li/LiFe$_{0.9}$Mg$_{0.1}$PO$_4$ cell, and also shows good cycling and
capacity of the cell. The performance shown after about
150 to 160 cycles is very good and shows that electrode
formulation LiFe$_{0.9}$Mg$_{0.1}$PO$_4$ performed significantly better
25   than the LiFePO$_4$. Comparing **Figure 3** (LiFePO$_4$) to **Figure**
6 (LiFe$_{0.9}$Mg$_{0.1}$PO$_4$) it can be seen that the Fe/Mg-phosphate
maintains its capacity over prolonged cycling, whereas
the Fe-phosphate capacity fades significantly.

Figure 7 shows the results of the first
30   constant current cycling at 0.2 milliamps per square
centimeter between about 2.5 and 4.0 volts based upon
about 16 milligrams of the LiFe$_{0.8}$Mg$_{0.2}$PO$_4$ active material

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in the cathode (positive electrode). In an as prepared,
as assembled, initial condition, the positive electrode
active material is $LiFe_{0.8}Mg_{0.2}PO_4$. The lithium is
extracted from the $LiFe_{0.8}Mg_{0.2}PO_4$ during charging of the
5   cell. When fully charged, about 0.79 units of lithium
have been removed per formula unit. Consequently, the
positive electrode active material corresponds to
$LiFe_{0.8}Mg_{0.2}PO_4$ where x appears to be equal to about 0.79,
when the cathode material is at 4.0 volts versus Li/Li^+.
10   The extraction approximately 140 milliamp hours per gram
corresponding to about 2.2 milliamp hours based on 16
milligrams active material. Next, the cell is discharged
whereupon a quantity of lithium is re-inserted into the
$LiFe_{0.8}Mg_{0.2}PO_4$. The re-insertion corresponds to
15   approximately 122 milliamp hours per gram proportional to
the insertion of essentially all of the lithium. The
bottom of the curve corresponds to approximately 2.5
volts. The total cumulative specific capacity over the
entire cycle is 262 mAhr/g.

20   Referring to **Figure 8**, there is shown data for
the final product $LiFe_{0.9}Ca_{0.1}PO_4$, prepared from Fe_2O_3 and
$Ca(OH)_2$ by Reaction 3. Its $CuK\alpha$ x-ray diffraction
pattern contained all of the peaks expected for this
material as shown in **Figure 8**. The pattern evident in
25   **Figure 8** is consistent with the single phase olivine
phosphate compound, $LiFe_{0.9}Ca_{0.1}PO_4$. This is evidenced by
the position of the peaks in terms of the scattering
angle 2 θ (theta), x axis. The x-ray pattern showed no
peaks due to the presence of precursor oxides indicating
30   that the solid state reaction is essentially entirely
completed. Here the space group SG = Pnma (62) and the
lattice parameters from XRD refinement are consistent
with olivine. The values are a = 10.3240Å (0.0045), b =

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6.0042Å (0.0031); c = 4.6887Å (0.0020), cell volume = 290.6370Å (0.1807), zero = 0.702 (0.003), p = 3.62 g/cc, PFWHM = 0.18, and crystallite = 680Å. The x-ray pattern demonstrates that the product of the invention was indeed

5   the nominal formula $LiFe_{0.9}Ca_{0.1}PO_4$.

   Figure 9 shows the results of the first constant current cycling at 0.2 milliamps per square centimeter between about 2.5 and 4.0 volts based upon about 18.5 milligrams of the $LiFe_{0.8}Ca_{0.2}PO_4$ active

10 material in the cathode (positive electrode). In an as prepared, as assembled, initial condition, the positive electrode active material is $LiFe_{0.8}Ca_{0.2}PO_4$. The lithium is extracted from the $LiFe_{0.8}Ca_{0.2}PO_4$ during charging of the cell. When fully charged, about 0.71 units of

15 lithium have been removed per formula unit. Consequently, the positive electrode active material corresponds to $LiFe_{0.8}Ca_{0.2}PO_4$ where x appears to be equal to about 0.71, when the cathode material is at 4.0 volts versus Li/Li^+. The extraction represents approximately

20 123 milliamp hours per gram corresponding to about 2.3 milliamp hours based on 18.5 milligrams active material. Next, the cell is discharged whereupon a quantity of lithium is re-inserted into the $LiFe_{0.8}Ca_{0.2}PO_4$. The re-insertion corresponds to approximately 110 milliamp hours

25 per gram proportional to the insertion of nearly all of the lithium. The bottom of the curve corresponds to approximately 2.5 volts. The total specific cumulative capacity over the entire cycle is 233 mAhr/g.

   Figure 10 shows the results of the first

30 constant current cycling at 0.2 milliamps per square centimeter between about 2.5 and 4.0 volts based upon about 18.9 milligrams of the $LiFe_{0.8}Zn_{0.2}PO_4$ olivine active

50

material in the cathode (positive electrode). In an as
prepared, as assembled, initial condition, the positive
electrode active material is $LiFe_{0.8}Zn_{0.2}PO_4$, prepared from
Fe_2O_3 and $Zn_3(PO_4)_2$ by Reaction 4. The lithium is
5   extracted from the $LiFe_{0.8}Zn_{0.2}PO_4$ during charging of the
cell. When fully charged, about 0.74 units of lithium
have been removed per formula unit. Consequently, the
positive electrode active material corresponds to Li_{1-}
$_xFe0.8Zn0.2PO4$ where x appears to be equal to about 0.74,
10   when the cathode material is at 4.0 volts versus Li/Li^+.
The extraction represents approximately 124 milliamp
hours per gram corresponding to about 2.3 milliamp hours
based on 18.9 milligrams active material. Next, the cell
is discharged whereupon a quantity of lithium is re-
15   inserted into the $LiFe_{0.8}Zn_{0.2}PO_4$. The re-insertion
corresponds to approximately 108 milliamp hours per gram
proportional to the insertion of nearly all of the
lithium. The bottom of the curve corresponds to
approximately 2.5 volts.

20   Referring to **Figure 11**, the final product
LiV_2O_5, prepared by Reaction 5, appeared black in color.
Its $CuK\alpha$ x-ray diffraction pattern contained all of the
peaks expected for this material as shown in **Figure 11.**
The pattern evident in **Figure 11** is consistent with a
25   single oxide compound gamma-LiV_2O_5. This is evidenced by
the position of the peaks in terms of the scattering
angle 2 θ (theta), x axis. The x-ray pattern showed no
peaks due to the presence of precursor oxides indicating
that the solid state reaction is essentially entirely
30   completed.

            The x-ray pattern demonstrates that the product
of the invention was indeed the nominal formula gamma-

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LiV_2O_5. The term "nominal formula" refers to the fact
that the relative proportion of atomic species may vary
slightly on the order of 2 percent to 5 percent, or more
typically, 1 percent to 3 percent.

5   The LiV_2O_5 prepared as described immediately
above, was tested in an electrochemical cell. The cell
was prepared as described above and cycled with
performance as shown in **Figures 12 and 13**.

           Figure 12 shows the results of the first
10   constant current cycling at 0.2 milliamps per square
centimeter between about 2.8 and 3.8 volts based upon
about 15.0 milligrams of the LiV_2O_5 active material in
the cathode (positive electrode). In an as prepared, as
assembled, initial condition, the positive electrode
15   active material is LiV_2O_5. The lithium is extracted from
the LiV_2O_5 during charging of the cell. When fully
charged, about 0.93 unit of lithium had been removed per
formula unit. Consequently, the positive electrode
active material corresponds to $Li_{1-x}V_2O_5$ where x appears to
20   be equal to about 0.93, when the cathode material is at
3.8 volts versus Li/Li^+. The extraction represents
approximately 132 milliamp hours per gram corresponding
to about 2.0 milliamp hours based on 15.0 milligrams
active material. Next, the cell is discharged whereupon
25   a quantity of lithium is re-inserted into the LiV_2O_5. The
re-insertion corresponds to approximately 130 milliamp
hours per gram proportional to the insertion of
essentially all of the lithium. The bottom of the curve
corresponds to approximately 2.8 volts.

30   **Figure 13** presents data obtained by multiple
constant current cycling at 0.4 milliamp hours per square

52.

centimeter (C/2 rate) of the LiV_2O_5 versus lithium metal
counter electrode between 3.0 and 3.75 volts. Data for
two temperature conditions are shown, 23°C and 60°C.
Figure 13 is a two part graph with **Figure 13A** showing the
5   excellent rechargeability of the LiV_2O_5. **Figure 13B**
shows good cycling and capacity of the cell. The
performance shown up to about 300 cycles is good.

Referring to **Figure 14**, the final product
$Li_3V_2(PO_4)_3$, prepared by Reaction 6, appeared green/black
10   in color. Its CuKα x-ray diffraction pattern contained
all of the peaks expected for this material as shown in
Figure 14. The pattern evident in **Figure 14** is
consistent with a single phosphate compound $Li_3V_2(PO_4)_3$ of
the monoclinic, Nasicon phase. This is evidenced by the
15   position of the peaks in terms of the scattering angle 2
θ (theta), x axis. The x-ray pattern showed no peaks due
to the presence of precursor oxides indicating that the
solid state reaction is essentially entirely completed.

The x-ray pattern demonstrates that the product
20   of the invention was indeed the nominal formula
$Li_3V_2(PO_4)_3$. The term "nominal formula" refers to the fact
that the relative proportion of atomic species may vary
slightly on the order of 2 percent to 5 percent, or more
typically, 1 percent to 3 percent; and that substitution
25   of P and O may occur.

The $Li_3V_2(PO_4)_3$ prepared as described immediately
above, was tested in an electrochemical cell. The cell
was prepared as described above, using 13.8mg of active
material. The cell was prepared as described above and
30   cycled between about 3.0 and about 4.2 volts using the
EVS technique with performance as shown in **Figures 16 and**

17. **Figure 16** shows specific capacity versus electrode potential against Li. **Figure 17** shows differential capacity versus electrode potential against Li.

A comparative method was used to form
5    $Li_3V_2(PO_4)_3$. Such method was reaction without carbon and under H_2-reducing gas as described in U.S. Patent No. 5,871,866. The final product, prepared as per U.S. Patent No. 5,871,866, appeared green in color. Its CuKα x-ray diffraction pattern contained all of the peaks
10   expected for this material as shown in **Figure 15**. The pattern evident in **Figure 15** is consistent with a monoclinic Nasicon single phase phosphate compound $Li_3V_2(PO_4)_3$. This is evidenced by the position of the peaks in terms of the scattering angle 2 θ (theta), x
15   axis. The x-ray pattern showed no peaks due to the presence of precursor oxides indicating that the solid state reaction is essentially entirely completed. Chemical analysis for lithium and vanadium by atomic absorption spectroscopy showed, on a percent by weight
20   basis, 5.17 percent lithium and 26 percent vanadium. This is close to the expected result of 5.11 percent lithium and 25 percent vanadium.

The chemical analysis and x-ray patterns of **Figures 14 and 15** demonstrate that the product of **Figure**
25   **14** was the same as that of **Figure 15**. The product of **Figure 14** was prepared without the undesirable H_2 atmosphere and was prepared by the novel carbothermal solid state synthesis of the invention.

Figure 16 shows a voltage profile of the test
30   cell, based on the $Li_3V_2(PO_4)_3$ positive electrode active material made by the process of the invention and as

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characterized in **Figure 14.** It was cycled against a
lithium metal counter electrode. The data shown in
Figure 16 is based on the Electrochemical Voltage
Spectroscopy (EVS) technique. Electrochemical and
5   kinetic data were recorded using the Electrochemical
Voltage Spectroscopy (EVS) technique. Such technique is
known in the art as described by J. Barker in Synth, Met
28, D217 (1989); Synth. Met. 32, 43 (1989); J. Power
Sources, 52, 185 (1994); and Electrochemica Acta, Vol.
10   40, No. 11, at 1603 (1995). **Figure 16** clearly shows and
highlights the reversibility of the product. The positive
electrode contained about 13.8 milligrams of the
$Li_3V_2(PO_4)_3$ active material. The positive electrode
showed a performance of about 133 milliamp hours per gram
15   on the first discharge. In **Figure 16,** the capacity in,
and the capacity out are essentially the same, resulting
in essentially no capacity loss. **Figure 17** is an EVS
differential capacity plot based on **Figure 16.** As can be
seen from **Figure 17,** the relatively symmetrical nature of
20   peaks indicates good electrical reversibility, there are
small peak separations (charge/discharge), and good
correspondence between peaks above and below the zero
axis. There are essentially no peaks that can be related
to irreversible reactions, since all peaks above the axis
25   (cell charge) have corresponding peaks below the axis
(cell discharge), and there is essentially no separation
between the peaks above and below the axis. This shows
that the carbothermal method of the invention produces
high quality electrode material.

30   **Figure 18** presents data obtained by multiple
constant current cycling at 0.2 milliamp hours per square
centimeter of the $LiFe_{0.8}Mg_{0.2}PO_4$ versus lithium metal
counter electrode between 2.5 and 4.0 volts. **Figure 18**

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shows the excellent rechargeability of the
Li/LiFe$_{0.8}$Mg$_{0.2}$PO$_4$ cell, and also shows good cycling and
capacity of the cell. The performance shown after about
110 to 120 cycles at 23°C is very good and shows that

5   electrode formulation LiFe$_{0.8}$Mg$_{0.2}$PO$_4$ performed
significantly better than the LiFePO$_4$. The cell cycling
test at 60°C was started after the 23°C test and was
ongoing. Comparing **Figure 3** (LiFePO$_4$) to **Figure 18**
(LiFe$_{0.8}$Mg$_{0.2}$PO$_4$), it can be seen that the Fe/Mg-phosphate

10   maintains its capacity over prolonged cycling, whereas
the Fe-phosphate capacity fades significantly.

In addition to the above cell tests, the active
materials of the invention were also cycled against
insertion anodes in non-metallic, lithium ion, rocking

15   chair cells.

The lithium mixed metal phosphate and the
lithium metal oxide were used to formulate a cathode
electrode. The electrode was fabricated by solvent
casting a slurry of the treated, enriched lithium

20   manganese oxide, conductive carbon, binder, plasticizer
and solvent. The conductive carbon used was Super P (MMM
Carbon). Kynar Flex 2801® was used as the binder and
electronic grade acetone was used as a solvent. The
preferred plasticizer was dibutyl phthalate (DPB). The

25   slurry was cast onto glass and a free-standing electrode
was formed as the solvent was evaporated. In this
example, the cathode had 23.1mg LiFe$_{0.9}$Mg$_{0.1}$PO$_4$ active
material. Thus, the proportions are as follows on a
percent weight basis: 80% active material; 8% Super P

30   carbon; and 12% Kynar binder.

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A graphite counter electrode was prepared for
use with the aforesaid cathode. The graphite counter
electrode served as the anode in the electrochemical
cell. The anode had 10.8 mg of the MCMB graphite active
5   material. The graphite electrode was fabricated by
solvent casting a slurry of MCMB2528 graphite, binder,
and casting solvent. MCMB2528 is a mesocarbon microbead
material supplied by Alumina Trading, which is the U.S.
distributor for the supplier, Osaka Gas Company of Japan.
10 This material has a density of about 2.24 grams per cubic
centimeter; a particle size maximum for at least 95% by
weight of the particles of 37 microns; median size of
about 22.5 microns and an interlayer distance of about
0.336. As in the case of the cathode, the binder was a
15 copolymer of polyvinylidene difluoride (PVdF) and
hexafluoropropylene (HFP) in a wt. ratio of PVdF to HFP
of 88:12. This binder is sold under the designation of
Kynar Flex 2801®, showing it's a registered trademark.
Kynar Flex is available from Atochem Corporation. An
20 electronic grade solvent was used. The slurry was cast
onto glass and a free standing electrode was formed as
the casting solvent evaporated. The electrode
composition was approximately as follows on a dry weight
basis: 85% graphite; 12% binder; and 3% conductive
25 carbon.

A rocking chair battery was prepared comprising
the anode, the cathode, and an electrolyte. The ratio of
the active cathode mass to the active anode mass was
about 2.14:1. The two electrode layers were arranged
30 with an electrolyte layer in between, and the layers were
laminated together using heat and pressure as per the
Bell Comm. Res. patents incorporated herein by reference
earlier. In a preferred method, the cell is activated

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with EC/DMC solvent in a weight ratio of 2:1 in a
solution containing 1 M $LiPF_6$ salt.

Figures 19 and 20 show data for the first four
complete cycles of the lithium ion cell having the
5      $LiFe_{0.9}Mg_{0.1}PO_4$ cathode and the MCMB2528 anode. The cell
comprised 23.1mg active $LiFe_{0.9}Mg_{0.1}PO_4$ and 10.8mg active
MCMB2528 for a cathode to anode mass ratio of 2.14. The
cell was charged and discharged at 23°C at an approximate
C/10 (10 hour) rate between voltage limits of 2.50 V and
10   3.60 V. The voltage profile plot (Figure 19) shows the
variation in cell voltage versus time for the
$LiFe_{0.9}Mg_{0.1}PO_4$/MCMB2528 lithium ion cell. The symmetrical
nature of the charge-discharge is clearly evident. The
small degree of voltage hysteresis between the charge and
15   discharge processes is evidence for the low overvoltage
in the system, which is very good. Figure 20 shows the
variation of $LiFe_{0.9}Mg_{0.1}PO_4$ specific capacity with cycle
number. Clearly, over the cycles shown, the material
demonstrates good cycling stability.

20   Figure 21 shows data for the first three
complete cycles of the lithium ion cell having the gamma-
LiV_2O_5 cathode and the MCMB2528 anode. The cell prepared
was a rocking chair, lithium ion cell as described above.
The cell comprised 29.1mg gamma-LiV_2O_5 cathode active
25   material and 12.2mg MCMB2528 anode active material, for a
cathode to anode mass ratio of 2.39. As stated earlier,
the liquid electrolyte used was EC/DMC (2:1) and 1M
$LiPF_6$. The cell was charged and discharged at 23°C at an
approximate C/10 (10 hour) rate between voltage limits of
30   2.50 V and 3.65 V. The voltage profile plot (Figure 21)
shows the variation in cell voltage versus time for the
LiV_2O_5/MCMB2528 lithium ion cell. The symmetrical nature

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of the charge-discharge is clearly evident. The small
degree of voltage hysteresis between the charge and
discharge processes is evidence for the low overvoltage
in the system, which is very good.

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In summary, the invention provides new
compounds $Li_aMI_bMII_c(PO_4)_d$ and gamma-LiV_2O_5 by new methods
which are adaptable to commercial scale production. The
$Li_1MI_{1-y}MII_yPO_4$ compounds are isostructural olivine
10   compounds as demonstrated by XRD analysis. Substituted
compounds, such as $LiFe_{1-y}Mg_yPO_4$ show better performance
than $LiFePO_4$ unsubstituted compounds when used as
electrode active materials. The method of the invention
utilizes the reducing capabilities of carbon along with
15   selected precursors and reaction conditions to produce
high quality products suitable as electrode active
materials or as ion conductors. The reduction capability
of carbon over a broad temperature range is selectively
applied along with thermodynamic and kinetic
20   considerations to provide an energy-efficient, economical
and convenient process to produce compounds of a desired
composition and structure. This is in contrast to known
methods.

Principles of carbothermal reduction have been
25   applied to produce pure metal from metal oxides by
removal of oxygen. See, for example, U.S. Patent Nos.
2,580,878, 2,570,232, 4,177,060, and 5,803,974.
Principles of carbothermal and thermal reduction have
also been used to form carbides. See, for example, U.S.
30   Patent Nos. 3,865,745 and 5,384,291; and non-oxide
ceramics (see U.S. Patent No. 5,607,297). Such methods
are not known to have been applied to form lithiated
products or to form products without oxygen abstraction

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from the precursor. The methods described with respect to
the present invention provide high quality products which
are prepared from precursors which are lithiated during
the reaction without oxygen abstraction. This is a
5   surprising result. The new methods of the invention also
provide new compounds not known to have been made before.

For example, alpha-V_2O_5 is conventionally
lithiated electrochemically against metallic lithium.
Thus, alpha-V_2O_5 is not suitable as a source of lithium
10   for a cell. As a result, alpha-V_2O_5 is not used in an
ion cell. In the present invention, alpha-V_2O_5 is
lithiated by carbothermal reduction using a simple
lithium-containing compound and the reducing capability
of carbon to form a gamma-LiV_2O_5. The single phase
15   compound, gamma-LiV_2O_5 is not known to have been directly
and independently prepared before. There is not known to
be a direct synthesis route. Attempts to form it as a
single phase resulted in a mixed phase product containing
one or more beta phases and having the formula $Li_xV_2O_5$
20   with $0 < x \leq 0.49$. This is far different from the
present single phase gamma-$Li_xV_2O_5$ with x equal to one, or
very close to one. The flexibility of the process of the
present invention is such that it can be conducted over a
wide temperature range. The higher the temperature, the
25   more quickly the reaction proceeds. For example, at
650°C, conversion of alpha-V_2O_5 to gamma-LiV_2O_5 occurs in
about one hour, and at 500° it takes about 8 hours.
Here, about one quarter (1/4) atomic unit of carbon is
used to reduce one atomic unit of vanadium, that is,
30     $V^{+5}V^{+5}$ to $V^{+5}V^{+4}$. The predominate reaction is C to CO_2
where for each atomic unit of carbon at ground state
zero, a plus 4 oxidation state results. Correspondingly,
for each 1/4 atomic unit of carbon, one atomic unit of

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vanadium is reduced from V^{+5} to V^{+4}. (See Reaction 5).
The new product, gamma-LiV_2O_5 is air-stable and suitable
as an electrode material for an ion cell or rocking chair
battery.

5   The convenience and energy efficiency of the
present process can also be contrasted to known methods
for forming products under reducing atmosphere such as H_2
which is difficult to control, and from complex and
expensive precursors. In the present invention, carbon
10   is the reducing agent, and simple, inexpensive and even
naturally occurring precursors are useable. For example,
it is possible to produce $LiFePO_4$ from Fe_2O_3, a simple
common oxide. (See Reaction 1b). The production of
$LiFePO_4$ provides a good example of the thermodynamic and
15   kinetic features of the method. Iron phosphate is
reduced by carbon and lithiated over a broad temperature
range. At about 600°C, the C to CO_2 reaction
predominates and takes about a week to complete. At
about 750°C, the C to CO reaction predominates and takes
20   about 8 hours to complete. The C to CO_2 reaction
requires less carbon reductant but takes longer due to
the low temperature kinetics. The C to CO reaction
requires about twice as much carbon, but due to the high
temperature reaction kinetics, it proceeds relatively
25   fast. In both cases, the Fe in the precursor Fe_2O_3 has
oxidation state +3 and is reduced to oxidation (valence)
state +2 in the product $LiFePO_4$. The C to CO reaction
requires that ½ atomic unit of carbon be used for each
atomic unit of Fe reduced by one valence state. The CO
30   to CO_2 reaction requires that 1/4 atomic unit of carbon
be used for each atomic unit of Fe reduced by one valence
state.

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The active materials of the invention are also characterized by being stable in an as-prepared condition, in the presence of air and particularly humid air. This is a striking advantage, because it

5   facilitates preparation of and assembly of battery cathodes and cells, without the requirement for controlled atmosphere. This feature is particularly important, as those skilled in the art will recognize that air stability, that is, lack of degradation on

10 exposure to air, is very important for commercial processing. Air-stability is known in the art to more specifically indicate that a material does not hydrolyze in presence of moist air. Generally, air-stable materials are also characterized by Li being extracted

15 therefrom above about 3.0 volts versus lithium. The higher the extraction potential, the more tightly bound the lithium ions are to the host lattice. This tightly bound property generally confers air stability on the material. The air-stability of the materials of the

20 invention is consistent with the stability demonstrated by cycling at the conditions stated herein. This is in contrast to materials which insert Li at lower voltages, below about 3.0 volts versus lithium, and which are not air-stable, and which hydrolyze in moist air.

25 While this invention has been described in terms of certain embodiments thereof, it is not intended that it be limited to the above description, but rather only to the extent set forth in the following claims.

The embodiments of the invention in which an

30 exclusive property or privilege is claimed are defined in the following claims.

What Is Claimed Is:

1. A compound represented by the nominal general formula $LiFe_{1-y}M_yPO_4$ where $0 < y < 0.5$ and M is at least one selected from the group consisting of Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, and mixtures thereof.

2. The compound of claim 1 where $0 < y \leq 0.2$.

3. The compound of claim 1 having the nominal formula $LiFe_{1-y}Mg_yPO_4$.

4. The compound of claim 1 having the nominal formula $LiFe_{0.9}Mg_{0.1}PO_4$.

5. The compound of claim 1 having the nominal formula $LiFe_{1-y}Ca_yPO_4$.

6. The compound of claim 1 having the nominal formula $LiFe_{0.9}Ca_{0.1}PO_4$.

7. The compound of claim 1 having the nominal formula $LiFe_{1-y}Zn_yPO_4$.

8. The compound of claim 1 having the nominal formula $LiFe_{0.9}Zn_{0.1}PO_4$.

9. The compound of claim 1 which has an olivine structure.

10. A compound having the nominal general formula $LiMI_{1-x}MII_xPO_4$ where MI is selected from the group

consisting of Fe, Co, Ni, Mn, Cu, V, Sn, Ti, Cr, and
mixtures thereof, and MII is selected from the group
consisting of Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, and
mixtures thereof, and where y is greater than zero and
less than one.

11.   An olivine compound having the nominal
general formula $LiMI_{1-y}MII_yPO_4$ where MI is at least one
transition metal selected from Groups 4 to 11 inclusive
of the Periodic Table and has a +2 valence state, MII is
at least one metallic element which is selected from
Groups 2, 12, and 14 of the Periodic Table and has a +2
valence state, and where
$0 < y < 1$.

12.   The compound of claim 11 wherein MI is
selected from the group consisting of V, Cr, Mn, Fe, Co,
Cu, and mixtures thereof.

13.   The compound of claim 11 wherein MII is
selected from the group consisting of Mg, Ca, Ba, Zn, and
mixtures thereof.

14.   An electrode comprising a binder, an
electrically conductive carbonaceous material, and an
active material represented by the nominal general
formula $LiFe_{1-y}M_yPO_4$ where $0 < y < 0.5$ and M is at least
one selected from the group consisting of Mg, Ca, Zn, Sr,
Pb, Cd, Sn, Ba, Be, and mixtures thereof.

15.   The electrode of claim 14 wherein said
active material is a compound where $0 < y \leq 0.2$.

16.   The electrode of claim 14 wherein said active material is a compound having the nominal formula $LiFe_{1-y}Mg_yPO_4$.

17.   The electrode of claim 14 wherein said active material is a compound having the nominal formula $LiFe_{0.9}Mg_{0.1}PO_4$.

18.   The electrode of claim 14 wherein said active material is a compound having the nominal formula $LiFe_{1-y}Ca_yPO_4$.

19.   The electrode of claim 14 wherein said active material is a compound having the nominal formula $LiFe_{0.9}Ca_{0.1}PO_4$.

20.   The electrode of claim 14 wherein said active material is a compound having the nominal formula $LiFe_{1-y}Zn_yPO_4$.

21.   The electrode of claim 14 wherein said active material is a compound having the nominal formula $LiFe_{0.9}Zn_{0.1}PO_4$.

22.   The electrode of claim 14 wherein said active material has an olivine structure.

23.   An electrode comprising a binder, an electrically conductive carbonaceous material and an active material which is an olivine compound represented by the nominal general formula $LiMI_{1-y}MII_yPO_4$ where MI is at least one transition metal selected from Groups 4 to 11 inclusive of the Periodic Table and has a +2 valence state, MII is at least one metallic element which is

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selected from Groups 2, 12, and 14 of the Periodic Table
and has a +2 valence state, and where $0 < y < 1$.

24. The electrode of claim 23 wherein MI is
selected from the group consisting of V, Cr, Mn, Fe, Co,
Cu, and mixtures thereof.

25. The electrode of claim 23 wherein MII is
selected from the group consisting of Mg, Ca, Ba, Zn, and
mixtures thereof.

26. A lithium ion battery comprising:
        a first electrode having an active
material represented by the nominal general formula
$LiFe_{1-y}M_yPO_4$ where $0 < y < 0.5$ and M is at least one
selected from the group consisting of Mg, Ca, Zn, Sr, Pb,
Cd, Sn, Ba, Be, and mixtures thereof;
        a second electrode which is a counter-
electrode to said first electrode; and
        an electrolyte between said electrodes.

27. The battery of claim 26 wherein said
active material is a compound where $0 < y \leq 0.2$.

28. The battery of claim 26 wherein said
active material is a compound having the nominal formula
$LiFe_{1-y}Mg_yPO_4$.

29. The battery of claim 26 wherein said
active material is a compound having the nominal formula
$LiFe_{0.9}Mg_{0.1}PO_4$.

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30. The battery of claim 26 wherein said active material is a compound having the nominal formula $LiFe_{1-y}Ca_yPO_4$.

31. The battery of claim 26 wherein said active material is a compound having the nominal formula $LiFe_{0.9}Ca_{0.1}PO_4$.

32. The battery of claim 26 wherein said active material is a compound having the nominal formula $LiFe_{1-y}Zn_yPO_4$.

33. The battery of claim 26 wherein said active material is a compound having the nominal formula $LiFe_{0.9}Zn_{0.1}PO_4$.

34. The battery of claim 26 wherein said active material has an olivine structure.

35. A lithium ion battery comprising:

a first electrode having an active material which is an olivine compound represented by the nominal general formula $LiMI_{1-y}MII_yPO_4$ where MI is at least one transition metal selected from Groups 4 to 11 inclusive of the Periodic Table and has a +2 valence state, MII is at least one metallic element which is selected from Groups 2, 12, and 14 of the Periodic Table and has a +2 valence state, and where $0 < y < 1$;

a second electrode which is a counter-electrode to said first electrode; and

an electrolyte between said electrodes.

36.   The battery of claim 35 wherein MI is
selected from the group consisting of V, Cr, Mn, Fe, Co,
Cu, and mixtures thereof.

37.   The battery of claim 35 wherein MII is
selected from the group consisting of Mg, Ca, Ba, Zn, and
mixtures thereof.

38.   A compound represented by the nominal
formula LiV_2O_5 and having an orthorhombic crystal
structure with a = 9.7 ± 0.2Å, b = 3.6 ± 0.2Å and c =
10.6 ± 0.2Å.

39.   The compound of claim 38 which is prepared
by reacting vanadium pentoxide and lithium compound in
the presence of carbon at an elevated temperature
sufficient to form said single phase compound.

40.   An electrode comprising a binder, an
electrically conductive carbonaceous material and an
active material which is a compound represented by the
nominal general formula LiV_2O_5 and having an orthorhombic
crystal structure with a = 9.7 ± 0.2Å, b = 3.6 ± 0.2Å
and c = 10.6 ± 0.2Å.

41.   A lithium ion battery comprising:
          a first electrode having an active
material which is a compound represented by the nominal
formula LiV_2O_5 and having orthorhombic crystal structure
which a = 9.7 ± 0.2Å, b = 3.6 ± 0.2Å and c = 10.6 ±
0.2Å;

          a second electrode which is a counter-
electrode to said first electrode; and

          an electrolyte between said electrodes.

Figure 1

2S1036A1 (LiFePO₄)

bars refer to simulated pattern
from refined cell parameters
SG = Pnma (62)
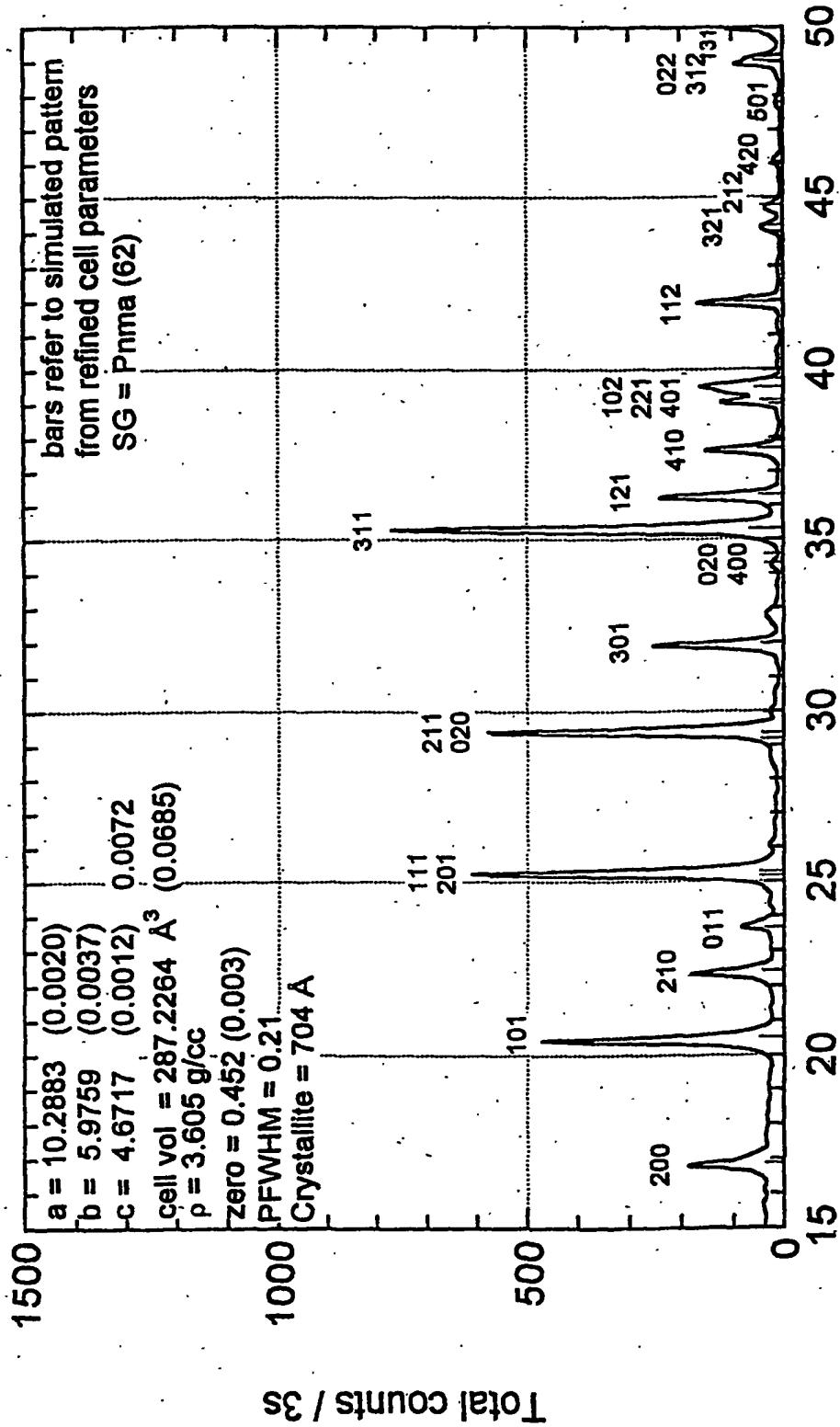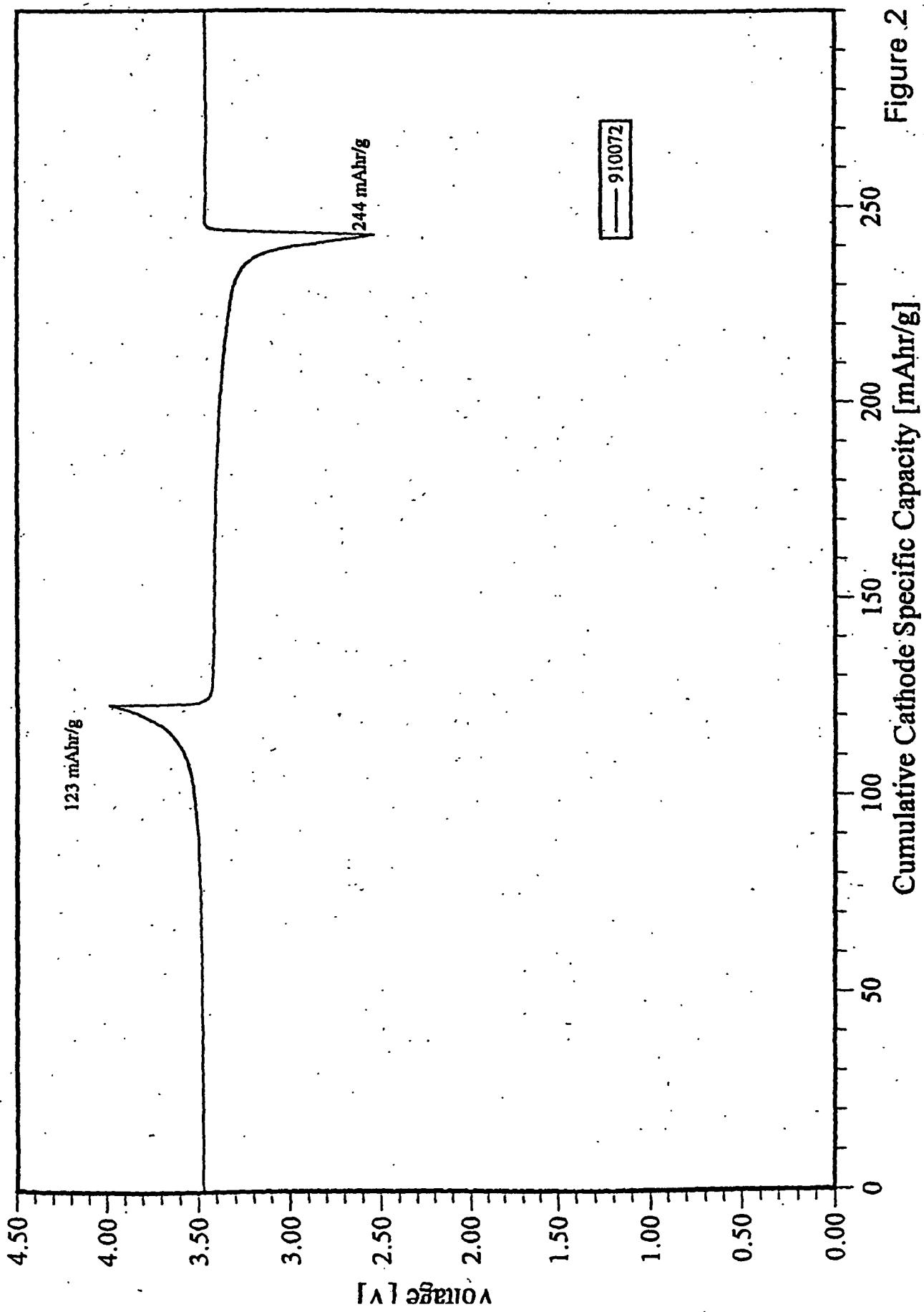
Figure 2

Carbothermal LiFePO4 vs Li
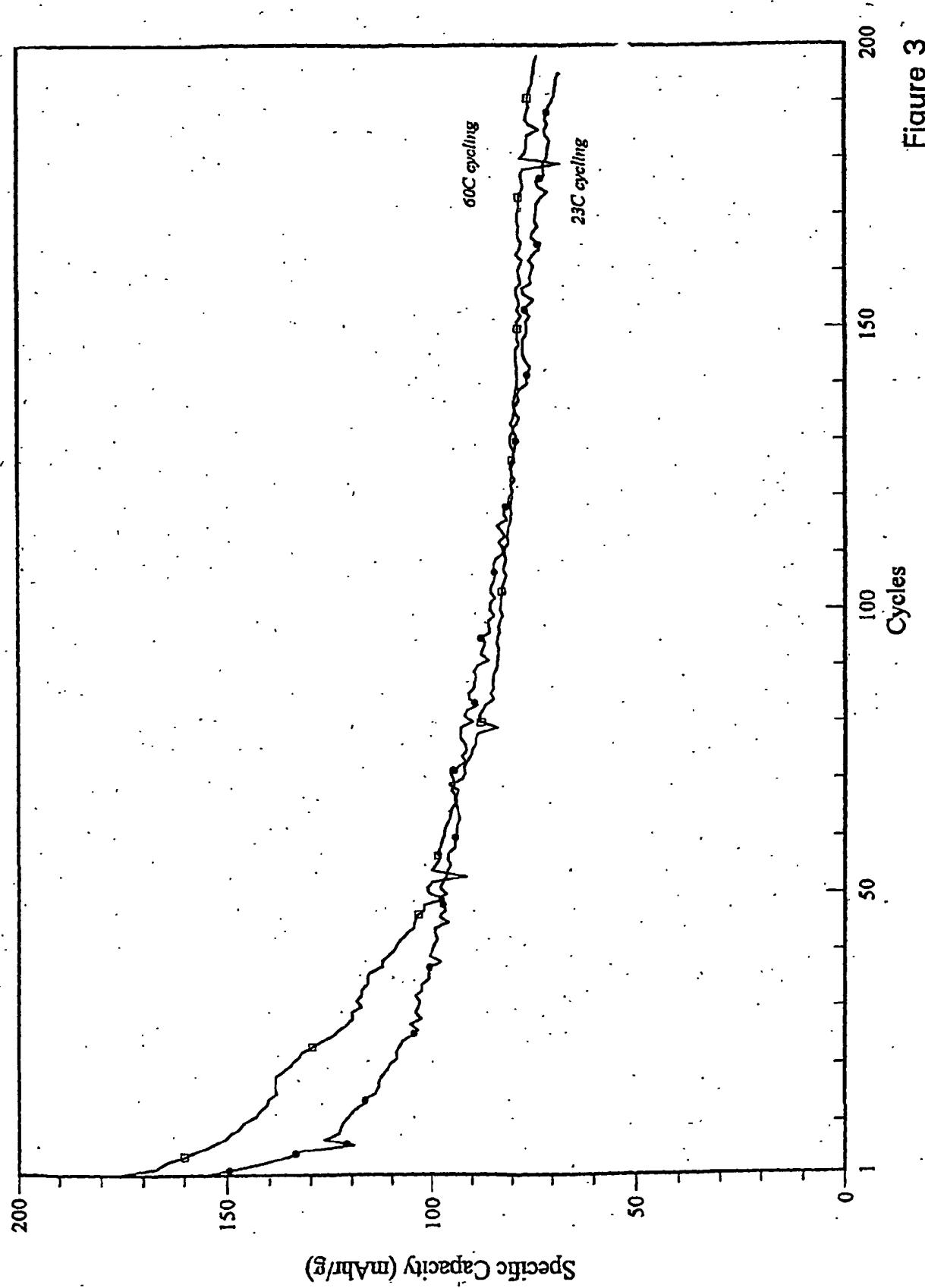
Figure 3
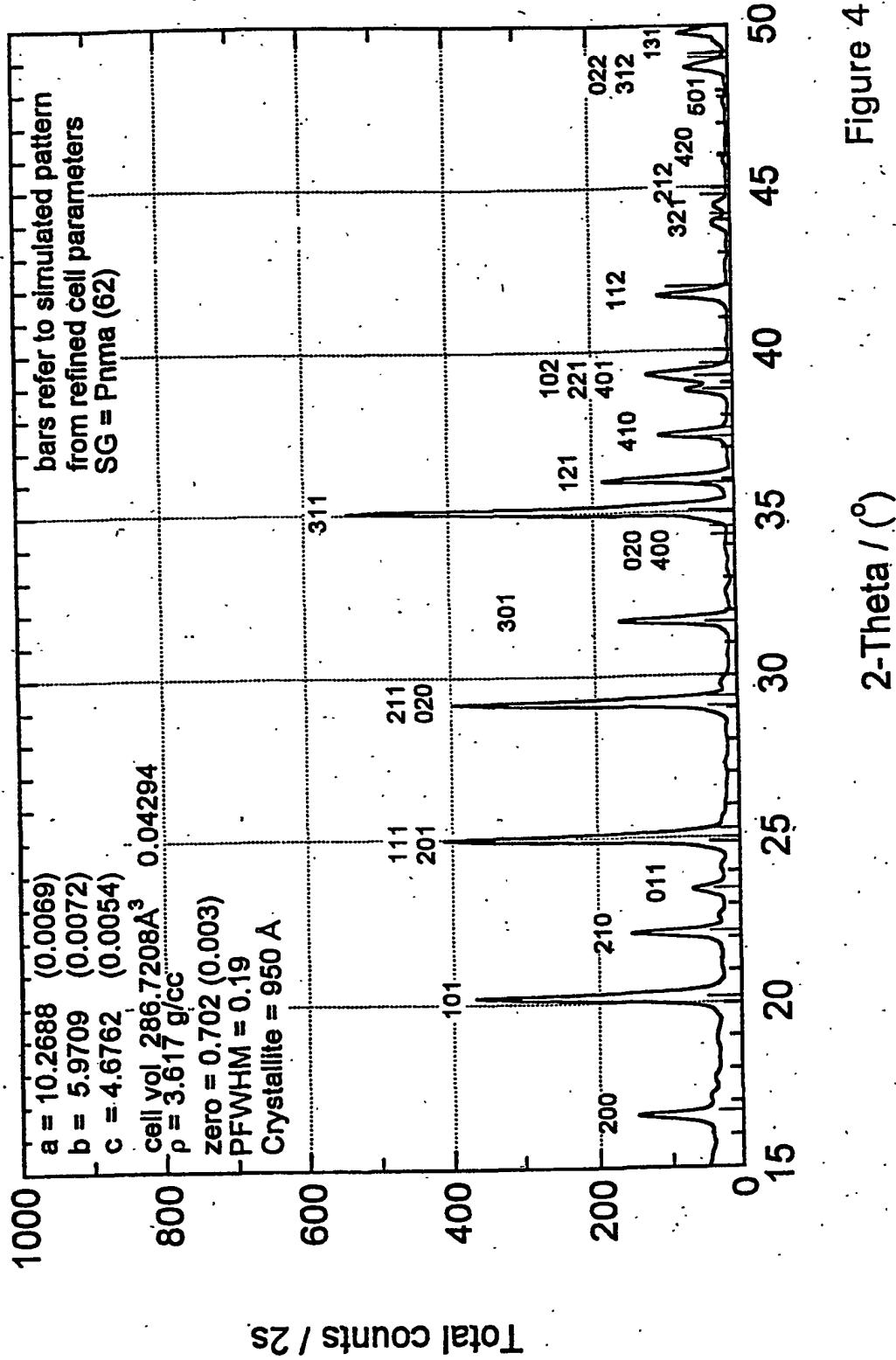
Figure 4

LiFe0.9Mg0.1PO4 2.5 - 4.0 V

150 mAhr/g

296 mAhr/g

910310

Cumulative Cathode Specific Capacity [mAhr/g]

Voltage [V]
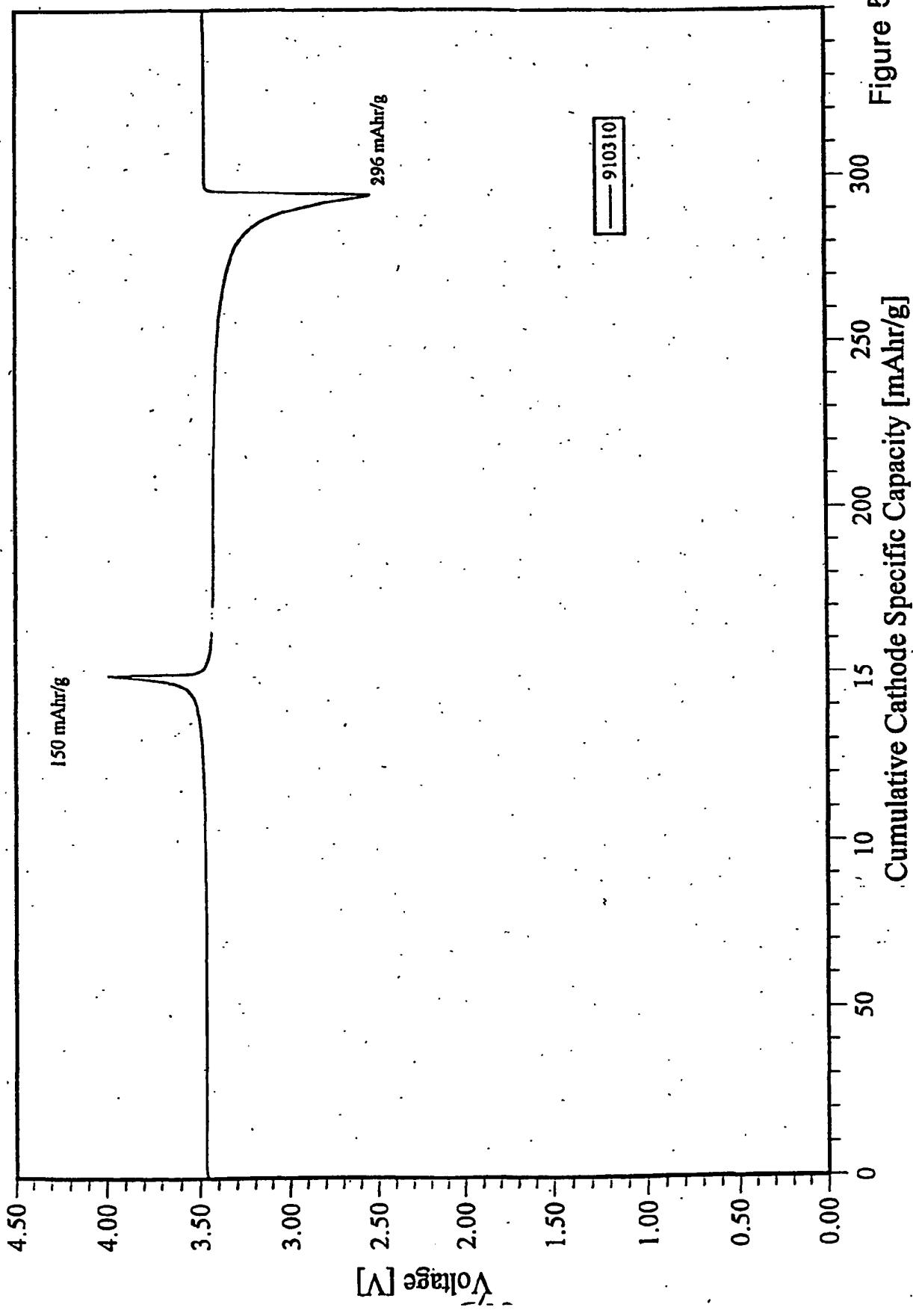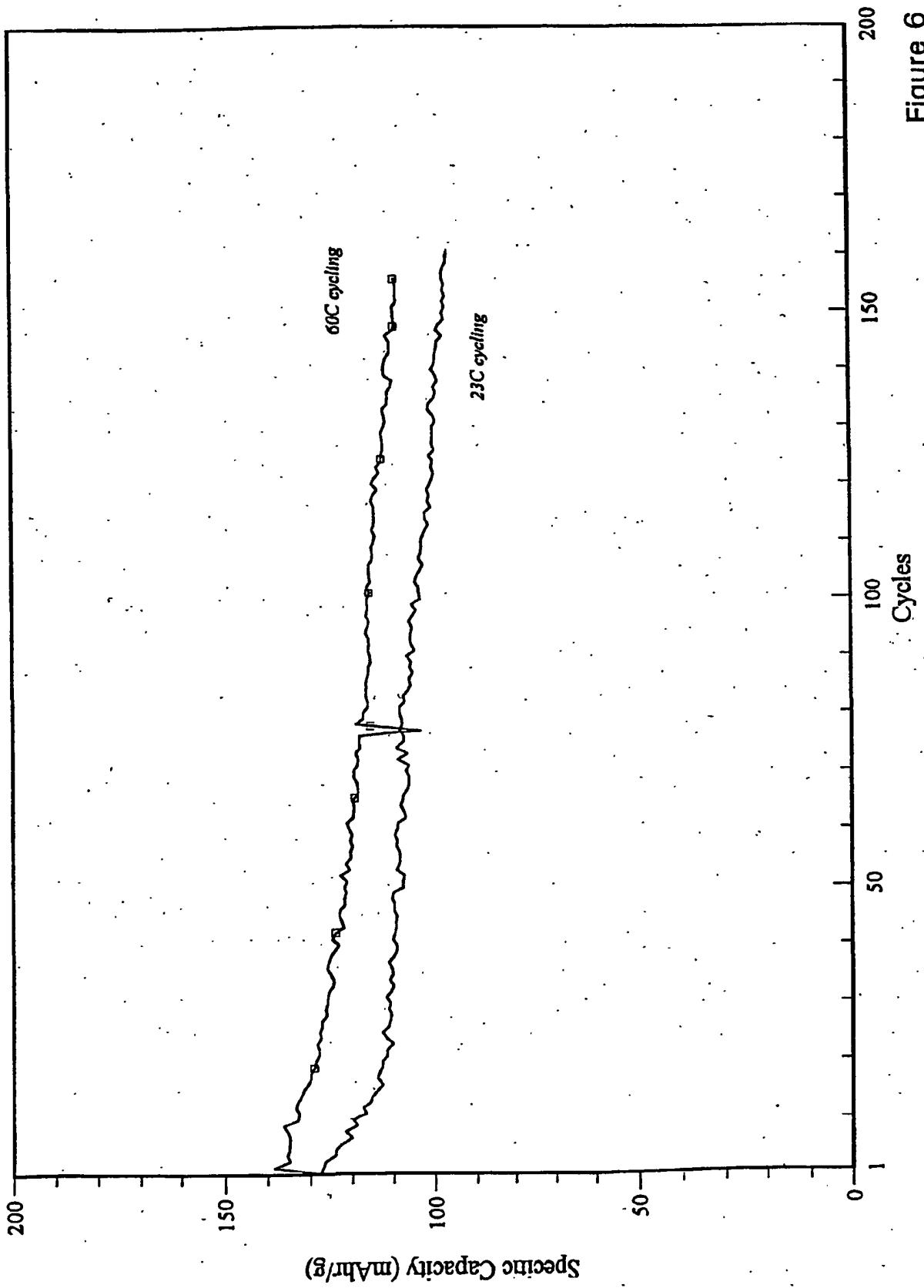
Figure 5

Figure 6

LiFe0.8Mg0.2PO4 2.5 - 4.0 V
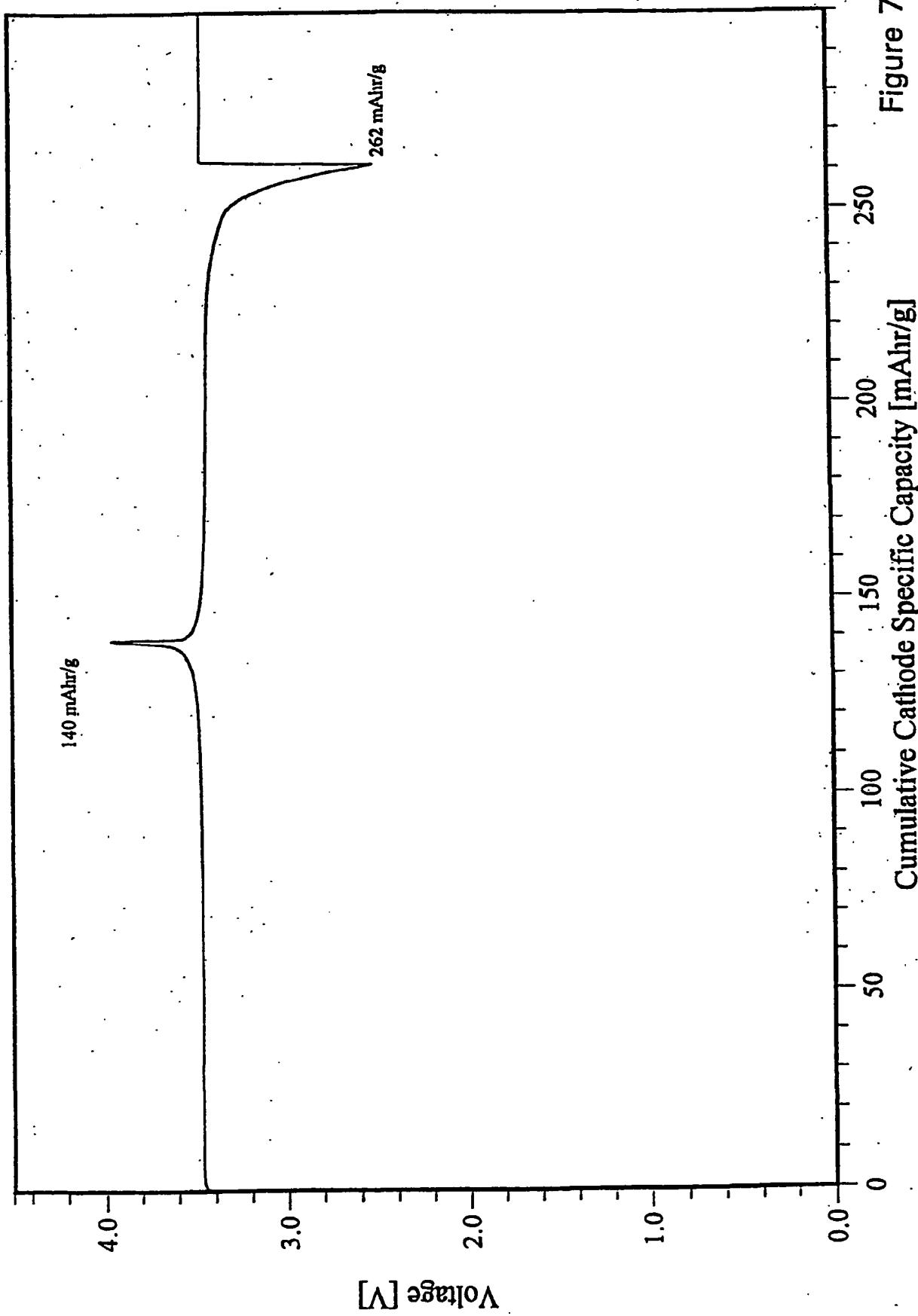
Figure 7

1S0937A1 (LiFe$_{0.9}$Ca$_{0.1}$PO$_4$)
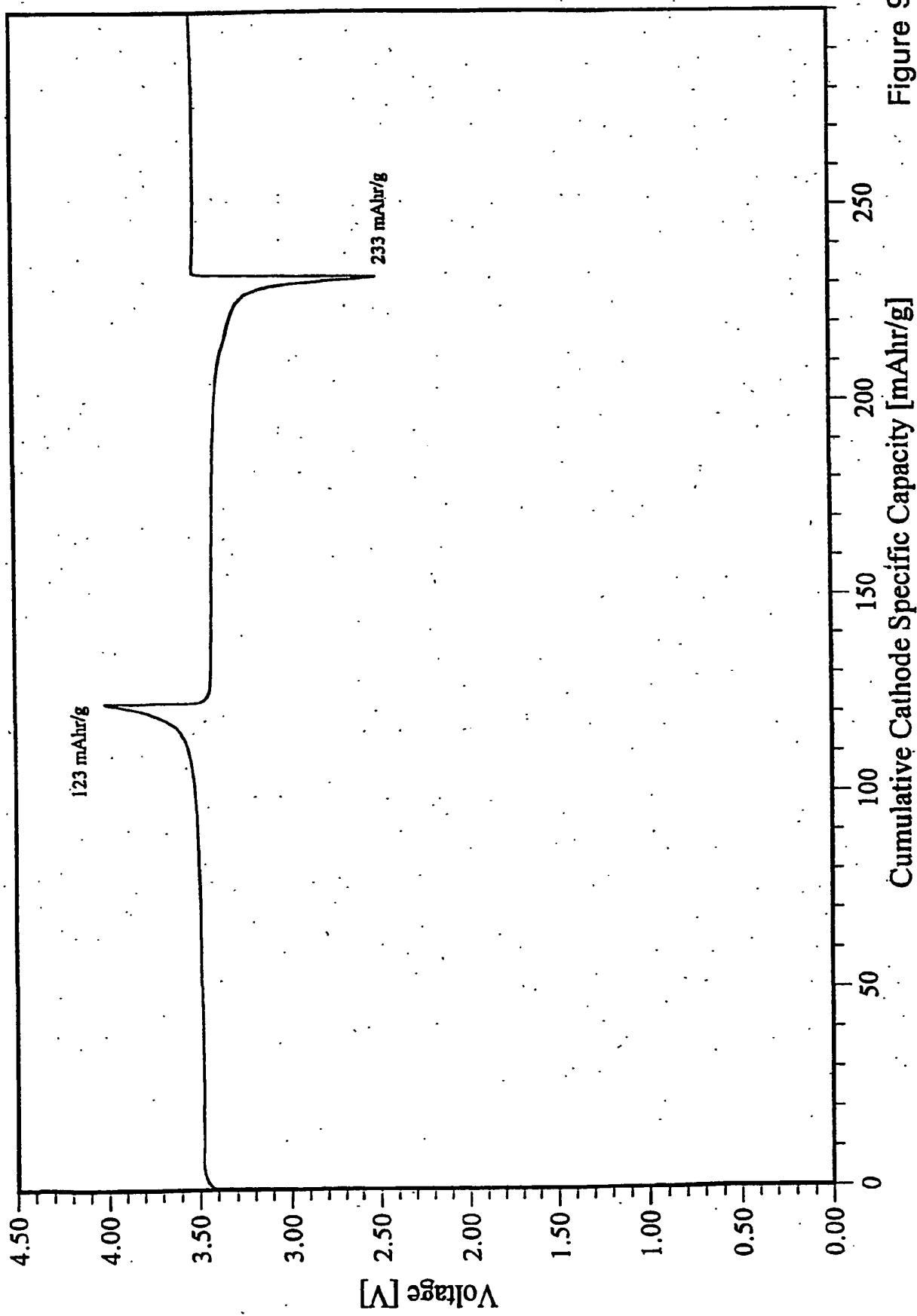
bars refer to simulated pattern
from refined cell parameters
SG = Pnma (62)

a = 10.3240 (0.0045)
b = 6.0042 (0.0031)
c = 4.6887 (0.0020)

cell Volume = 290.6370Å^3 (0.1807)
zero = 0.702 (0.003)

ρ = 3.62 g/cc
PFWHM = 0.18
Crystallite = 680

Figure 8

LiFe0.8Ca0.2PO4 2.5 - 4.0 V
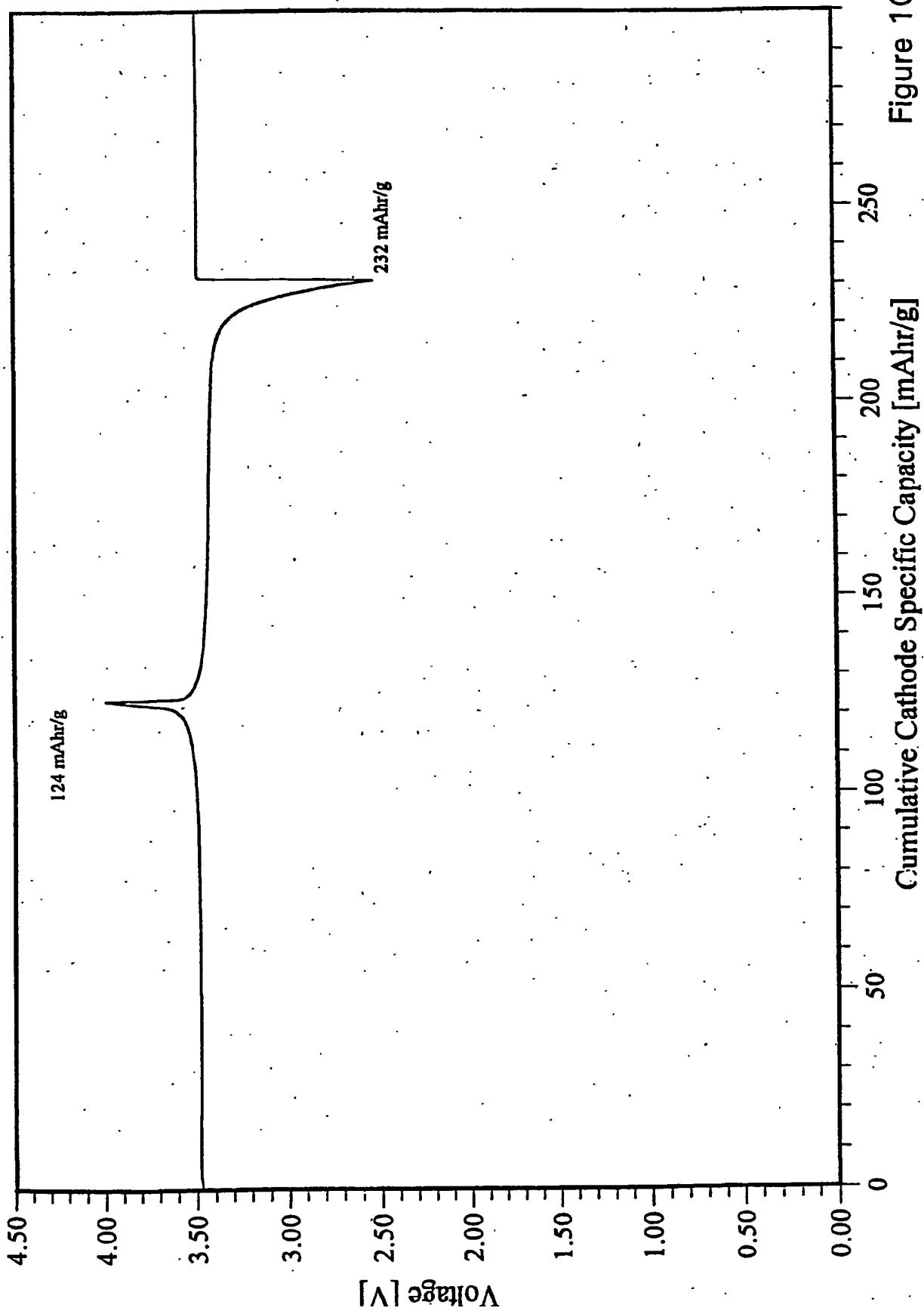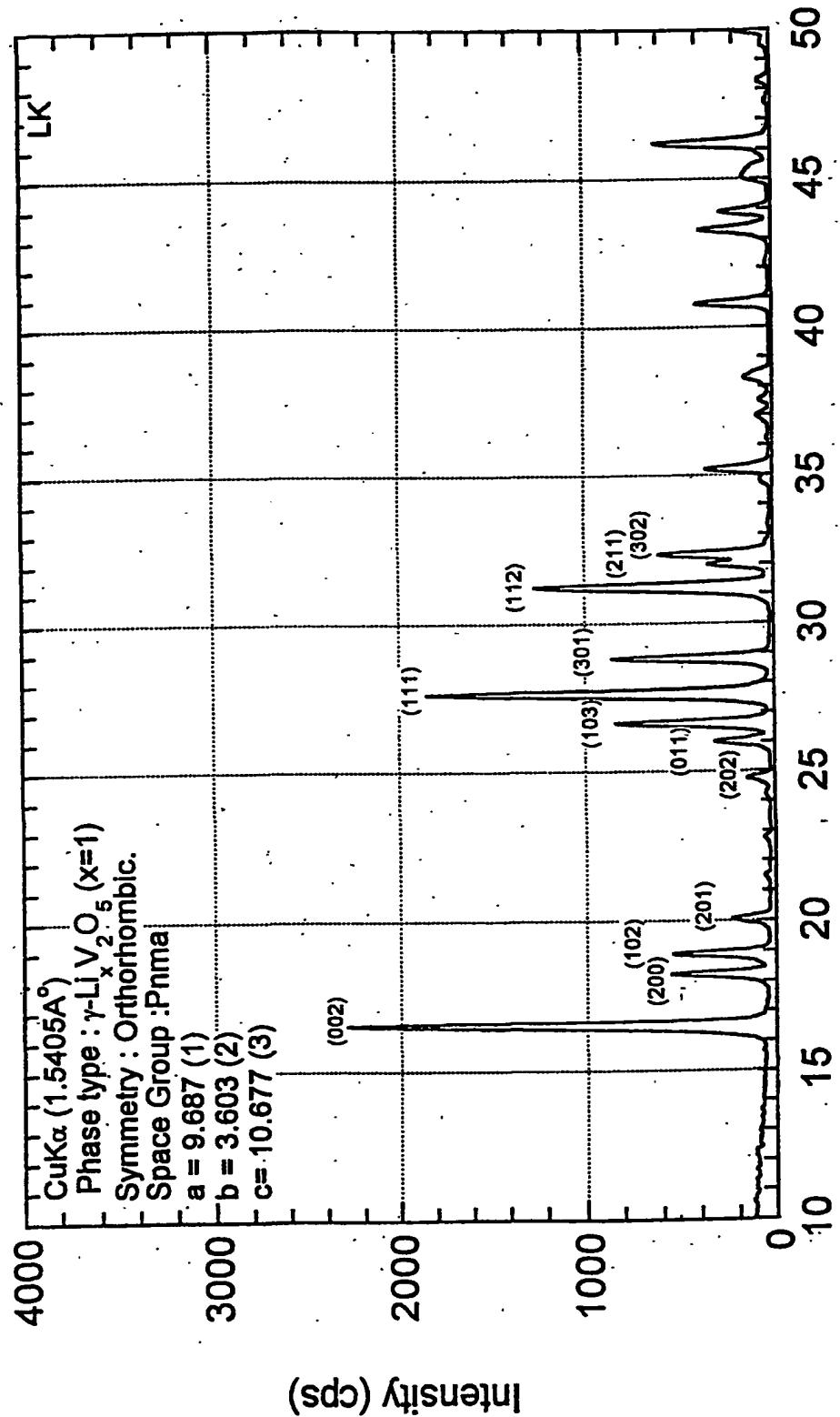
Figure 9

Figure 10

Figure 11

gamma-LiV2O5 Synthesized by Carbothermal Reduction Method

132 mAhr/g
3.8 Volts

262 mAhr/g
2.8 Volts

Voltage [V]

Cumulative Cathode Specific Capacity [mAhr/g]
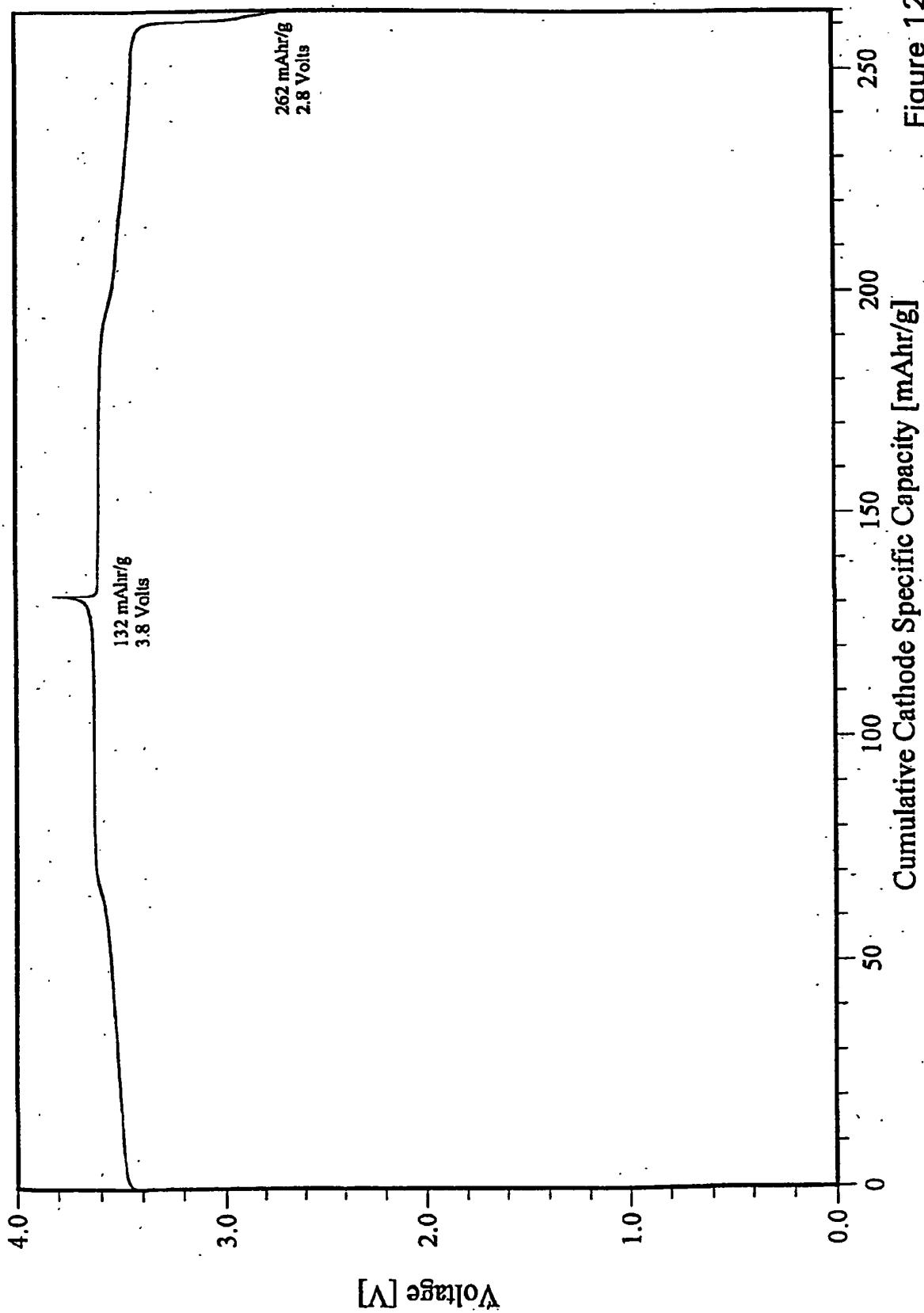
Figure 12

Figure 13

Figure 14

Figure 15

Li3V2(PO4)3 Synthesis by Carbothermal Reduction Method 13.8 mg active
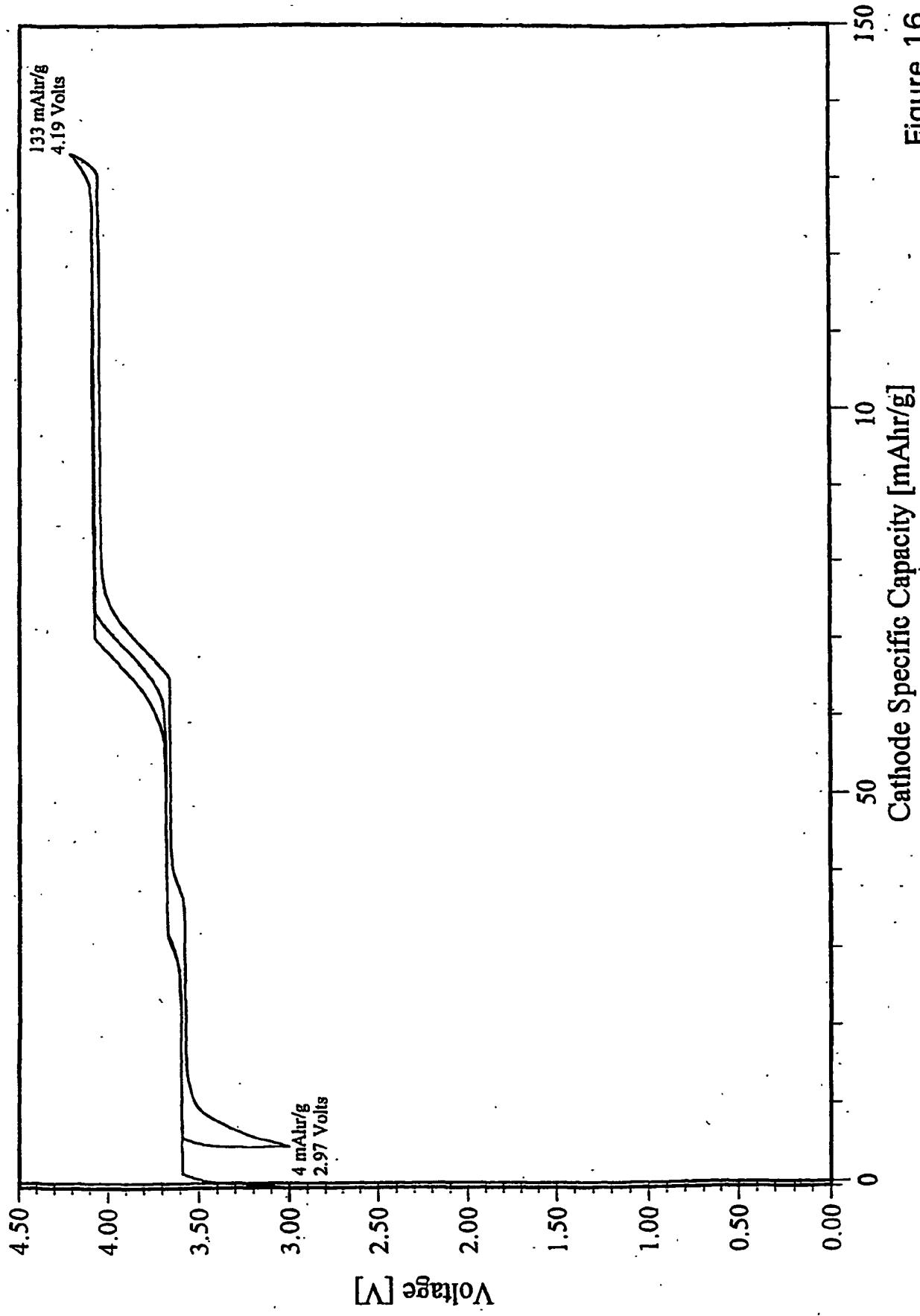
Figure 16

Li3V2(PO4)3 Synthesis by Carbothermal Reduction Method
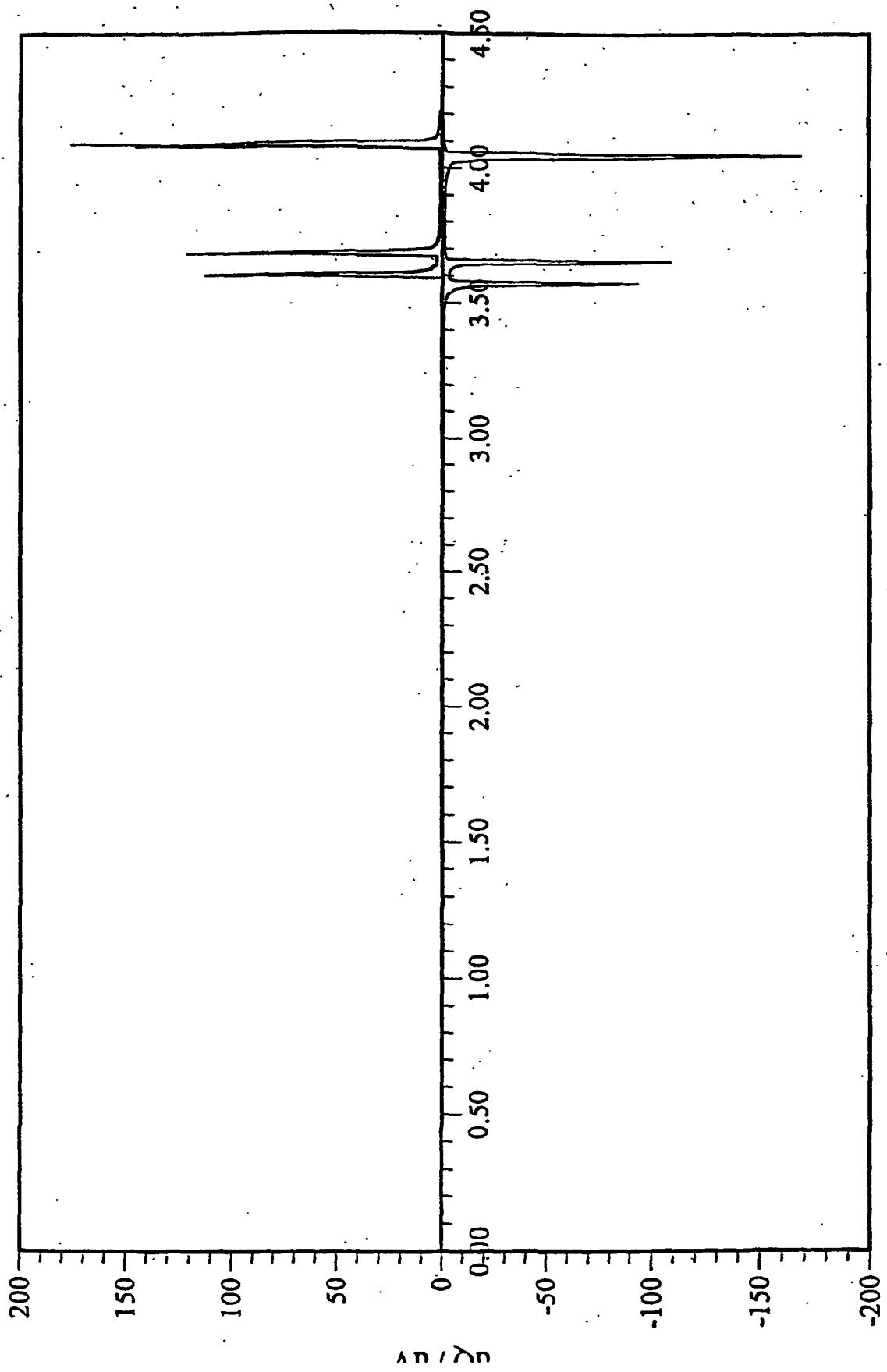
Figure 17

Voltage [V]
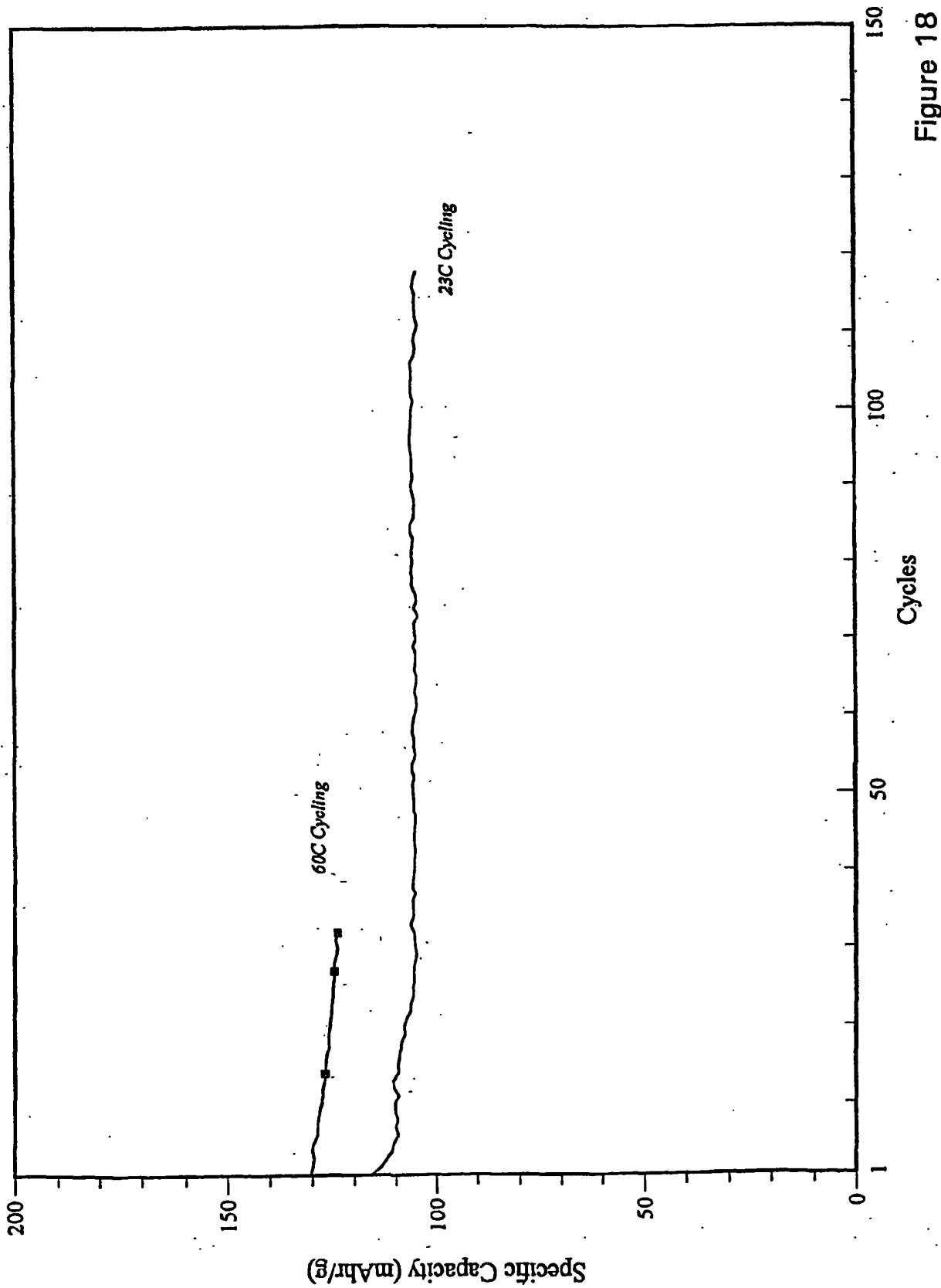
Figure 18

Voltage Profile for LiMg0.1Fe0.9PO4 vs MCMB
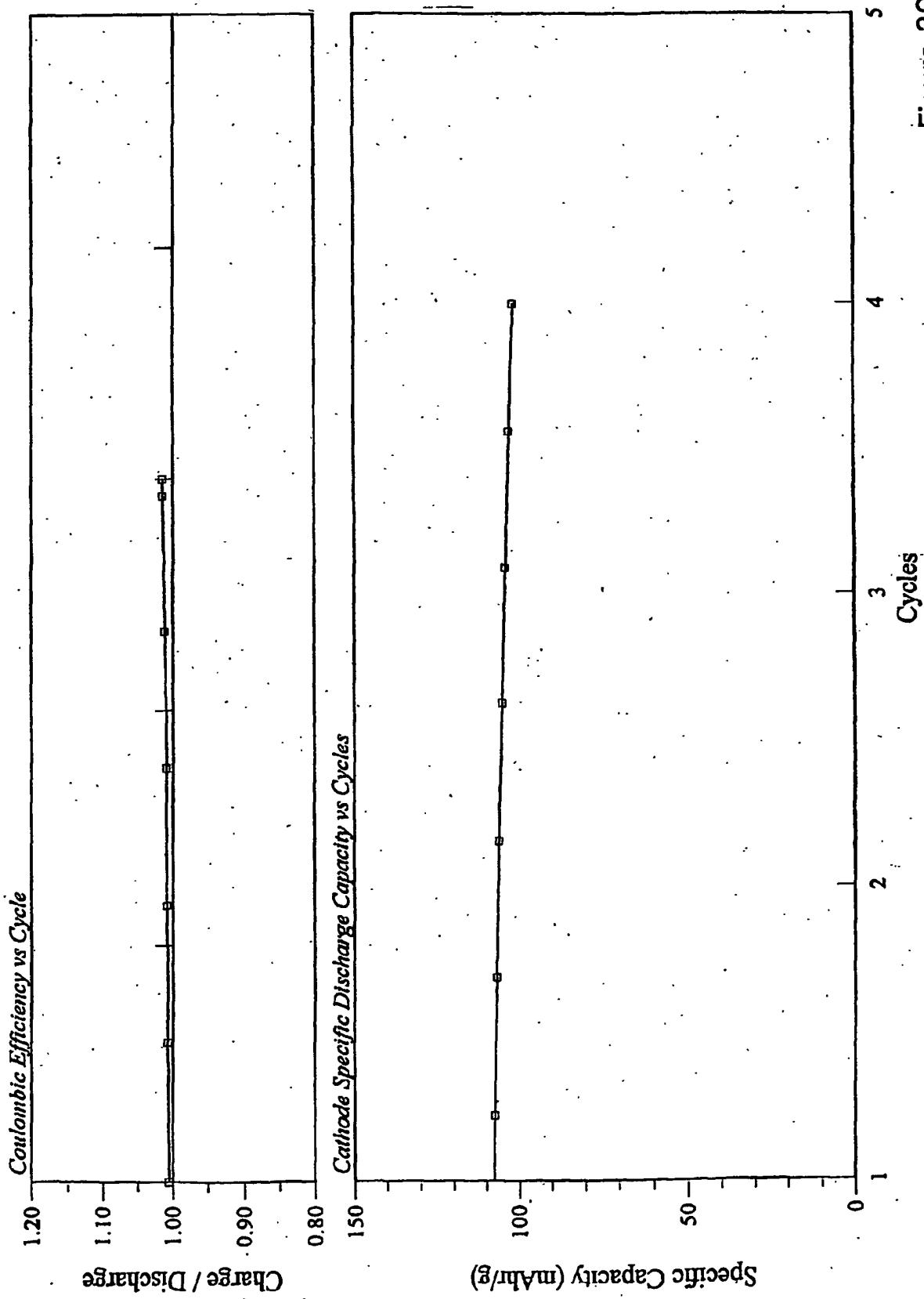
Figure 19

Figure 20

Carbothermal LiV2O5/MCMB2528 2.5-3.65 V
gamma-LiV$_2$O$_5$
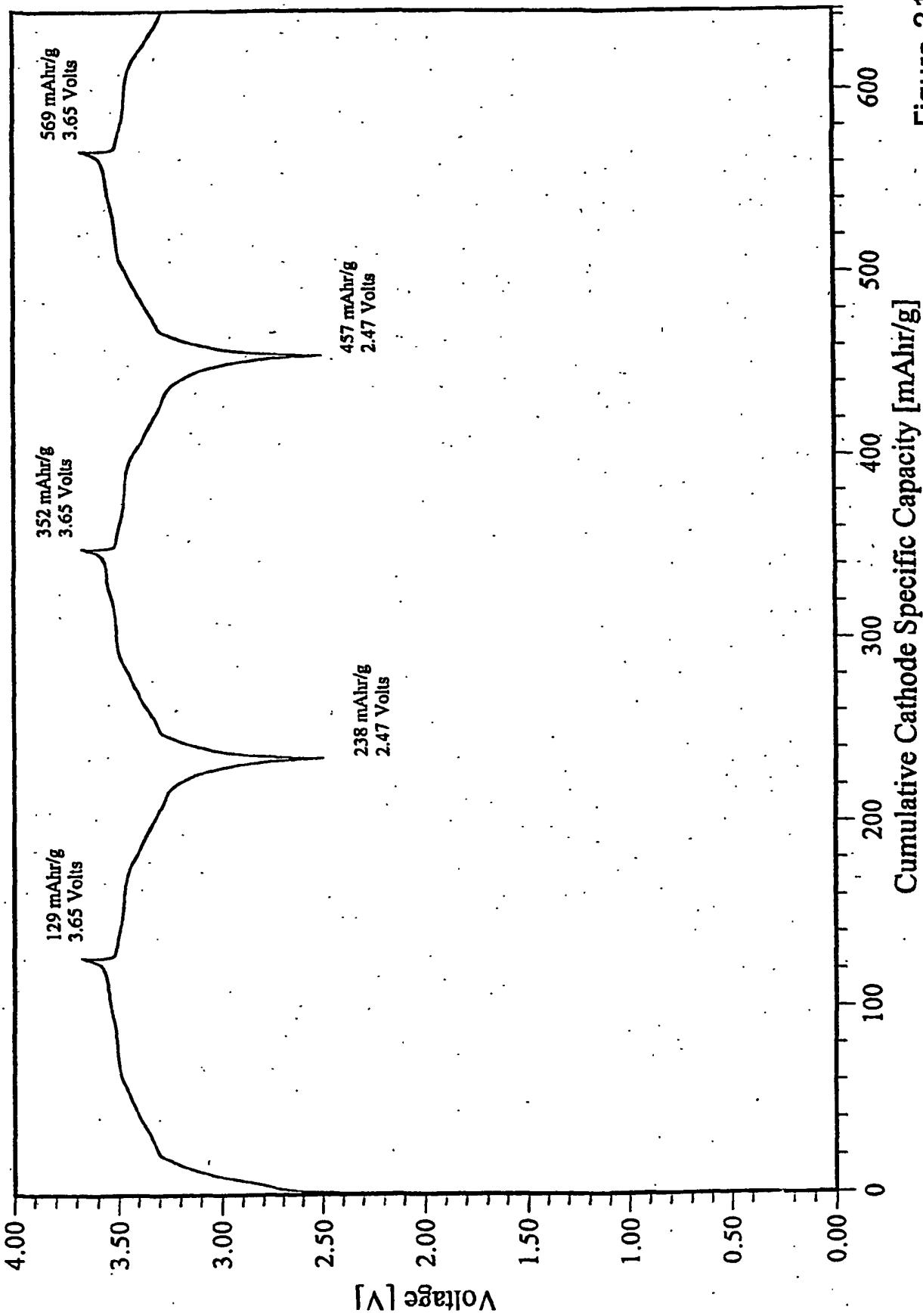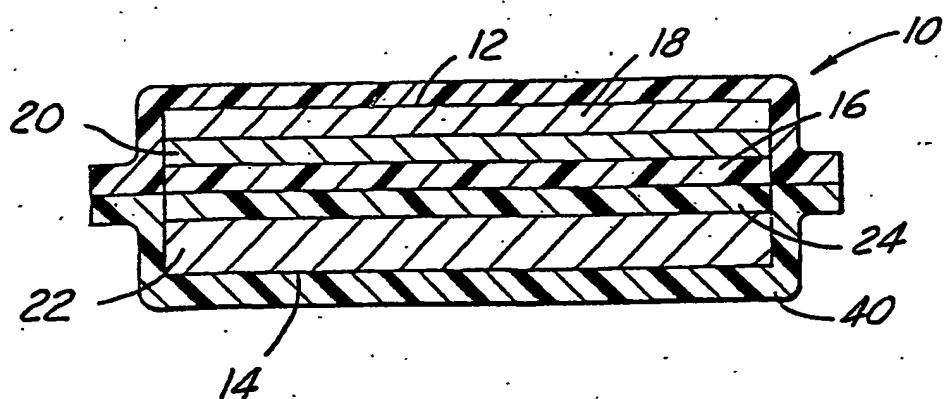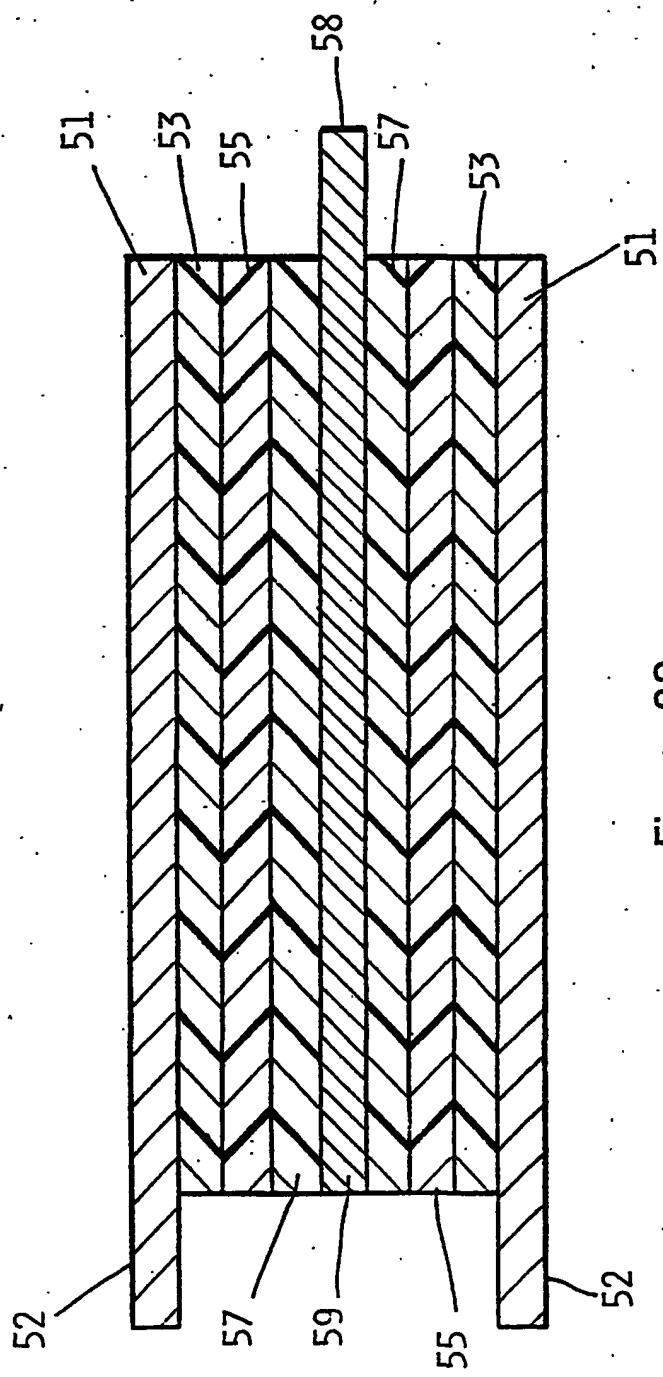
129 mAhr/g
3.65 Volts

352 mAhr/g
3.65 Volts

569 mAhr/g
3.65 Volts

238 mAhr/g
2.47 Volts

457 mAhr/g
2.47 Volts

Voltage [V]

Cumulative Cathode Specific Capacity [mAhr/g]

Figure 21

Figure 22

Figure 23

INTERNATIONAL SEARCH REPORT

Box I   Observations where certain laims were f und unsearchable (Continuati n of it m 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II   Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

> see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest   ☐ The additional search fees were accompanied by the applicant's protest.

☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   H01M4/48   H01M10/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7   H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP 1 049 182 A (HYDRO QUEBEC) 2 November 2000 (2000-11-02) example 11	10-14, 23,35-37
X	BOUNTINAUD P ET AL: "THE SOLID SOLUTION BALI1-XCUXPO4 (ASPIRE <0.5): AN EXAMPLE OF CU+ SINGLE-ION LUMINESCENCE IN OXIDE INSULATORS" JOURNAL OF MATERIALS CHEMISTRY,GB,THE ROYAL SOCIETY OF CHEMISTRY, CAMBRIDGE, vol. 6, no. 3, 1 March 1996 (1996-03-01), pages 381-384, XP000589539 ISSN: 0959-9428 the whole document	10-13

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| X | Further documents are listed in the continuation of box C. | | X | Patent family members are listed in annex. |

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 May 2001	08. 06.01

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax (+31–70) 340–3016	Engl, H

INTERNATIONAL SEARCH REPORT

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 04, 30 April 1999 (1999-04-30) & JP 11 025983 A (JAPAN STORAGE BATTERY CO LTD), 29 January 1999 (1999-01-29) abstract	10-13, 23-25, 35-37
X	DE 40 24 409 A (GEISMAR GUENTER ;HUND FRANZ DR (DE); WESTPHAL ULRICH DR (DE)) 6 February 1992 (1992-02-06) table 3	10-13
Y	PATENT ABSTRACTS OF JAPAN vol. 018, no. 091 (E-1508), 15 February 1994 (1994-02-15) & JP 05 299101 A (SANYO ELECTRIC CO LTD), 12 November 1993 (1993-11-12) abstract	1-37
A	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 09, 30 July 1999 (1999-07-30) & JP 11 111295 A (JAPAN STORAGE BATTERY CO LTD), 23 April 1999 (1999-04-23) abstract	1-37
Y	US 5 871 866 A (BARKER JEREMY ET AL) 16 February 1999 (1999-02-16) column 2, line 24 -column 3, line 1 column 5, line 7-10 claim 1	1-37
Y	T.J.BONAGAMBA ET AL: "7Li and 31P nuclear magnetic resonance studies of Li1-3xMgFexPO4" JOURNAL OF APPLIED PHYSICS, vol. 84, no. 1, 1 July 1998 (1998-07-01), pages 416-421, XP002164725 the whole document	1-37
Y	K.S.NANJUNDASWAMY ET AL: "Synthesis, redox potential evaluation and electrochemical characteristics of NASICON-related 3D framework compounds" SOLID STATE IONICS, vol. 92, 1996, pages 1-10, XP002164726 the whole document	1-37
A	J. GOPALAKRISHNAN: "V2(PO4)3: A novel NASICON-type Vanadium Phosphate" CHEMISTRY OF MATERIALS, vol. 4, no. 4, 7 August 1992 (1992-08-07), pages 745-747, XP002164727 the whole document	1-37

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category°	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	MARTINEZ–JUAREZ A, ET AL.: "Relationship between Activation Energy and Bottleneck Size for Li+ Ion Conduction in NASICON Materials of Composition LiMM'(PO4)3; M,M'=Ge, Ti, Sn., Hf" J. PHYS. CHEM., vol. 102, 1998, pages 372–375, XP002164949 page 373: Experimental Section page 375: Table 1	10
X	US 5 496 663 A (WALK CHARLES R ET AL) 5 March 1996 (1996-03-05) claims	38–41
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A	COCCIANTELLI J M ET AL: "On the delta @rarr gamma irreversible transformation in Li//V205 secondary batteries" SOLID STATE IONICS,NL,NORTH HOLLAND PUB. COMPANY. AMSTERDAM, vol. 78, no. 1, 1 May 1995 (1995-05-01), pages 143–150, XP004050409 ISSN: 0167-2738 the whole document	38–41

FURTHER INFORMATION CONTINUED FROM   PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-37

   The compounds

   A $LiFe_{1-y}M_yPO_4$, where $0<y<0.5$ and M = Mg, Ca, Zn, Sr,Pb, Cd, Sn, Ba, Be

   B $LiMI_{1-y}MII_yPO_4$ where MI = Fe, Co, Ni, Mn, Cu, V, Sn, Ti, Cr
         and MII = Mg, Ca, Zn, Sr, Pb, CD, Sn, Ba, Be

   C $LiMI_{1-y}MII_yPO_4$ where MI is a transition metal from groups 4 - 11 in valence state +2 and MII is a metallic element selected form groups 1, 12 and 14 in valence state 2; and $0<y<1$.

   Electrodes comprising said compounds, a binder and an electrically conductive carbonaceous material.

   Li ion batteries comprising said electrodes, a counterelectrode and an electrolyte.

2. Claims: 38-41

   A compound LiV_2O_5 with an orthorhombic crystal structure with a=9.7, b=3.6 and c=10.6 A.

   Electrodes comprising said compound, a binder and an electrically conductive carbonaceous material.

   Li ion batteries comprising said electrodes, a counterelectrode and an electrolyte.

INTERNATIONAL SEARCH REPORT

information on patent family members

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